The Occurence of Thallium in Minerals in Japan

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Introduction

Thallium is one of the geochemically high dispertive elements.[1] Some minerals containing thallium as their principal constituent are known to be secondary minerals and very rare.[2] Besides its occurrence in these minerals, thallium is sometimes found concentrated in an intermixture of copper,[3] iron[4] and zinc[5] sulfide ores. Thus, the flue-dust and chamber muds in refineries or sulfuric acid factories processing these ores are rather important as a technical source of thallium as studied by many workers.

Prof. K. Kimura and Y. Koyama[6] have investigated the thallium content in about eighty minerals in Japan by their semi-quantitative spectroscopic method. The author together with the above had hoped to investigate further the occurrence of thallium in these minerals and ores. Results of about 30 samples spectroscopically tested by the above method proposed by the two workers and the results of some which were chemically determined by the authors' method by using hexammine cobalti-trichloride as precipitant[7] to thallium, will be reported here.

Experimental

Spectroscopic Test Thallium has been spectroscopically determined by the following table proposed by the two workers.

Experimental Conditions Spectrograph: E 2 Type Spectrograph, Adam Hilger Co. Ltd., London.

Electrode: Electrolyzed copper rod (diameter 3 mm.). Diameter of hole into which the sample is inserted is 1 mm. and depths, 3 to 4 mm.

Current: Gradually increased up to 7 amperes during the first 30 seconds, maintaining 7 amperes for 40 seconds.

Dry plate: Process, panchromatic, Fuji Photograph Ind. Co. Ltd., Japan.

Developing: Developed at 3 min., 18°C with a special developer for the process plate above mentioned.

Table 1.

Relation between thallium content and intensity of its spectrum line*

Wave length	Thallium content (%)			
Å	1	0.1	0.01	0.001
3775.7	s	s	s	w
3229.8	w	—	—	—
2921.5	w · w	—	—	—
2918.3	s	w	w · w	—
2826.2	w · w	—	—	—
2710.7	?	—	—	—
2709.3	w · w	—	—	—
2379.6	w	—	—	—

* Cited from the report by K. Kimura and Y. Koyama (*J. Chem. Soc. Japan*, **57**, 1190 (1936))

Analytical Test Some of these samples spectroscopically found abundant in thallium were analyzed chemically. The sample about 10 g. powdered (100 mesh), dried at 105°C and made into a solution with the acid mixture was then determined closely following the author's method.

Experimental results

Analytical results are shown in Table 2.

Conclusion

By comparing the spectroscopical with the analytical results, it may be stated that the method proposed by Prof. K. Kimura *et al* can be utilized as a rapid and good method of the determination of thallium. The author's method in testing ores is also satisfactory, being distinctive in that it is hazardless and speedy, a condition not known in any other method of the past.

V.M. Goldschmidt[8] had classified thallium as a chalkophile element, and it had been stated by Berg[9] that thallium occurs in zinc-blende and iron sulfide ore, concentrated from the hydrothermal rest-solution in geochemical crystallization. Though a large number of the sample has not as yet been tested, the same results have been obtained, being distinctively so with markasite and pyrite. But in copper sulfide ore, thallium is either not found at all or else found in a very small amount.

(1) Nordenskiöld, *Lieb. Ann.*, **145** 127 (1868); V. M. Goldschmidt, *Zeit. Kryst. Min.*, **30**, 272 (1898); Kréhlik, *Zeit. Kryst. Min.*, **51**, 379 (1912)

(2) Gmelin, Handbuch der anorganische Chemie 8 (1939)

(3) A. Lamy, *Lieb. Ann.*, **124**, 218 (1862); T. U. Phipson, *Compt. rend.*, **78**, 563 (1874); W. I. Vernadsky, Bl. Acad. Petersb., (6) **4**, 1139 (1910)

(4) W. Crooks, *J. Chem. Soc.*, **17**, 115 (1864); W. N. Hartley and H. Ramage, *J. Chem. Soc. Ind.*, **71**, 540 (1897);. I Noddack, *Angew. Chem.*, **49**, 835 (1936)

(5) W. T. Roepper, *Ann. J. Sci.*, (2) **35**, 421 (1863); F. Wöhler, *Lieb. Ann.*, **142**, 263 (1867); Y Murakami, This Bulletin, in press.

(6) K. Kimura and Y. Koyama, *J. Chem. Soc. Japan*, **57**, 1190 (1936)

(7) Y. Murakami, This Bulletin, in press.

(8) V. M. Goldschmidt, *Videnskapsselsk. Skr.* Nr. **3**, 55 (1923)

(9) G. Berg, "Das Vorkommen der chemischen Element auf der Erde," 262, Leipzig (1932)

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Table 2

Thallium content in minerals

	Sample	Occurrence	Line detected	Content: Spectroscopically	Content: Chemically	Other constituent (in order of intensity)
1.	Markasite	Mori, Yamagata Pref.	3775.72(s) 2918.32(w)	0.1 %	0.085 %	Fe, Si, Al.
2.	Markasite	Tomimoto Yamagata Pref.	——	——	——	Fe, Si.
3.	Enarzite	Shimokita Oage, Aomori Pref.	3775.72(s) 2918.32(w)	0.1	0.056	Fe, Si.
4.	Markasite No. 1	Shimokita Oage, Aomori Pref.	3775.72(s) 2918.32(w)	0.1	——	Fe, Bi, Pb, As, Mn.
5.	No. 2	„	3775.72(W.W)	0.1 to 0.01	——	Pb, Fe.
6.	No. 3	„	3775.72(s) 2918.32(?)	<0.1	——	Pb, Fe, As.
7.	No. 4	„	3775.72(s) 2918.32(?)	<0.1	——	Fe, Si.
8.	Pyrite	Ochiaizawa bed, Hanaoka, Akita Pref	not tested	——	0.007	
9.	Black ore	Nishikanon bed, Hanaoka, Akita Pref.	not tested	——	0.001	
10.	Markasite	Kamiyama bed, Hanaoka, Akita Pref.	not tested	——	0.125	
11.	Zinc blend	Yunohanazawa, Akita Pref.	3775.72 2918.32(w)	0.1 to 0.01	0.070	Zn, Si, Pb.
12.	Copper ore No. 1	Doyashiki Hanaoka, Akita Pref.	not tested	——	0.005	
13.	No. 2 concentrates	„	not tested	——	0.024	
14.	No. 3	„	not tested	——	0.003	
15.	Markasite (in brown coal)	Agi, Gifu Pref.	——	——	——	Fe, Si, Mg.
16.	Black ore	Owani, Aomori Pref.	——	——	——	Zn, Pb, Mg.
17.	Covelin	Masutomi, Yamanashi Pref.	3775.72(?)	<0.001	——	Cu, Si.
18.	Markasite	„	——	——	——	Fe, Si.
19.	Enarzite	„	——	——	——	Cu, As.
20.	Ruzonite	„	——	——	——	Cu, Sb, As, Sn.
21.	Pyrite	Nishikanon bed, Hanaoka, Akita Pref.	not tested	——	0.007	
22.	Bismuth ore	Togane, Gifu Pref.	3775.72(?)	<0.001	——	Bi, Mo, Ca, Pb, Al, W, Sn.
23.	Markasite	Masutomi, Yamanashi Pref.	3775.72 2918.32(w.w)	0.1	not tested	Fe, Si.
24.	Zinc blend No. 1	Okurazawa, Akita Pref.	3775.72(w.w)	0.001	——	Zn, Si, Na, Pb, Al.
25.	No. 2	„	3375.72(w.w)	0.001	——	Zn, Si, Na, Pb, Al.
26.	Bismuthinite	Ebisu, Gifu Pref.	——	——	——	
27.	Bithmuth ore	Hohen, Yamaguchi Pref.	——	——	——	Fe, Si, Mg.
28.	Nature Bismuth	Ebisu, Gifu Pref.	3775.72(w) 2918.32(w)	0.1 to 0.001	not tested	Bi, Al, Mo, W, Sn, Zn, Si, Ag, As.
29.	Lead ore No. 1	Taishu (Akusuidani); Nagasaki Pref.	——	——	——	Fe, Si, Pb, Mg.
30.	No. 2	Taishu (Sasu bed No. 6); Nagasaki Pref.	3775.72(?)	0.001	——	Fe, Zn, Pb, Mg.

Thallium in natural bismuth and its ore could not be found in Ebisu mine formerly reported by Prof. K. Kimura and K. Koyama as a source of abundant thallium in zinc-blende and others. On the contrary it is remarkable that these samples abundant in thallium have been found in the Northeastern District (Tohoku-Chiho) of Japan.

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Modified Colorimetric Determination of Copper with Sodium Diethyldithiocarbamate in the Presence of Hydroxylamine

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Introduction

Sodium diethyldithiocarbamate was at first used by Callan and Henderson[1] in the colorimetric determination of a small amount of copper. He was followed by several workers who had studied this colorimetric determination, and among them Conn *et al*[2] made a special study of the various colorimetric determinations of copper being used up to that period. He pointed out the experimental defect of each method of determination and recommended the use of the sodium diethyldithiocarbamate method as the most accurate. This method is to be followed after isolating the copper with hydrogen sulphide to avoid interference from other elements usually present in the sample to be tested. He reported that hydrogen sulfide separation is superior to the tedious and time-consuming electrolytic separation recommended by Grendel.[3] Yet unfortunately it was also reported unsatisfactory.[4]

Upon these results Sylvester and Lampitt[5] attempted the colorimetric determination of copper in milk with this same reagent after having extracted the copper with chloroform as dithizonate. But Nydahl[6] proposed the same method as Sylvester and Lampitt in determining copper in fats, using carbon tetrachloride in place of chloroform as an extractant. Thus this reagent, producing an intense golden yellow coloration when put into contact with any amount of copper in the solution, has been used as highly sensitive reagent in the determination of minute quantities of the element.

However it has one drawback in colorimetry in that, when extracted with some other organic solvents, it does not variate in degrees of coloration in direct proportion to the amount of copper present. To solve this difficulty organic solvents such as ether,[7] chloroform,[5] carbon tetrachloride,[8] amyl alcohol[9] and isoamyl alcohol[10] were proposed but none were satisfactory.

Such being the case, color comparison must be undertaken by a series of standard solutions treated in the same way or by the use of a Lovibond tintometer at the loss of accuracy and sensitivity of the reagent. But McFarlane[9] reported that the use of a Duboscqu colorimeter would, to some extent, produce color variations proportional to the amount present. Of course that is when the copper is extracted with amyl alcohol. However, unfortunately the results obtained by some workers could,[10][11] not prove this statement. Naturally the degree of coloration in the original aqueous solution strictly conforms with the Lambert-Beers' law as it does in the case of amyl alcohol and carbon tetrachloride solution being used as an extractant, provided that the specially made filter[12] is used. The use of such a filter, however, is not generally possible. On the other hand Nydhal explained in his report that his method in practice agrees with the law if shaken successively two or three hundreds times with carbon tetrachloride. However, the best accuracy cannot be expected. Though a highly sensitive reagent is used for the determination, this drawback is unavoidable being probably due to the difficulty of transferring the colored products completely into solvents.

This defect was, however, finally abolished by the application of a new method tried by the author using carbon tetrachloride as an extractant in the presence of hydroxylamine. The object of this report will therefore be to give some details on this new method.

Procedure Discussed

Color reaction Though sodium diethyl-

(1) T. Callan and J.A.R. Henderson, *Analyst*, **54**, 650 (1929)

(2) L.W. Conn, A.H. Johson, H. A. Trebler and V. Karprenko, *Ind. Eng. Chem. Anal. Ed.*, **7**, 15 (1935); R.W. Thatcher, *J. Am. Chem. Soc.*, **55**, 4524 (1933)

(3) F. Grendel. *Phrm. Weekblad.*, **67**, 913, 1343 (1930); *Z. Anal. Chem.* **97**, 47 (1934)

(4) Walker. *J. Assoc. Offici. Agr. Chem.*, **13**, 426 (1930)

(5) N.D. Sylvester and L.H. Lampitt. *Analyst*, **60**, 377 (1935)

(6) F. Nydahl, Z. *Anal. Chem.*, **116**, 315 (1939)

(7) S.L. Tompsett, *Biochem. J.*, **29**, 480 (1929)

(8) L.A. Haddock and N. Evers, *Analyst*, **57**, 495 (1932)

(9) McFarlane, *Biochem. J.*, **26**, 1022 (1932); *Z. Anal. Chem.*, **101**, 71 (1935)

(10) E.J. Caulson, *J. Assoc. Offici. Agr. Chem.*, **20**, 178 (1937)

(11) D.L. Drabkin, *J. Assoc. Offici. Agr. Chem.*, **21**, 202(1938); L.A. Haddock and N. Evers, *Analyst*, **57**, 495 (1932); c.f. O B. Winter, *J. Assoc. Offici. Agr. Chem.*, **19**, 359 (1936)

(12) D.L. Drabkin, sec foot-note (11)

dithiocarbamate is not exclusively active with copper, but reacts with such metals as Bi, Fe, Mn, Ni, Co, Cr, forming colored complexes and with Zn, Pb, Hg, Cd, Sb, Sn and Al becoming turbid, it nevertheless has been used for copper determination because of its high sensitivity. It is therefore necessary that copper be preliminarily separated from other metals to obtain the best results. After a comparative study of preliminary separation of copper, the author decided upon the use of dithizone in the basic solution containing some citrate after the Sandells' direction, details of which will be reported in the last communications. With the use of dithizone in carbon tetrachloride and the acid treatment with 0.01 N hydrochloric acid some of these interfering metals are avoided, for Sb, Sn, Al and Cr, do not react with dithizone and Pb, Zn and Cd perfectly separate into the acid solution being isolated from copper by treating the dithizonates with 0.01 N hydrochloric acid. The amount of Fe and Mn in this case is extremely small owing to the addition of citrate which prevents its reaction with dithizone. Even should they be present, 50 p.p.m. of each are permissible in a small amount of copper as 1 to 3 p. p. m.[5] Coloration with some other metals was studied, and E_γ was calculated from the results, meaning the extinction coefficient of 1 cm. of the solution when 1 γ of the element present in 1 ml. of the solution is measured. (Table 1)

Table 1

Sensitivity of some elements to sodium diethyldithiocarbamate

Ions	Cu	Mn	Co	Ni	Bi	Zn	Pb	Fe	Ti
E_γ	0.201	0.0000	0.0168	0.0081	0.0018	0.0040	0.0001	0.0007	0.0000
Color-reaction	Golden yellow	Pink (unstable)	Dull green	Greenish yellow	Yellow (precipitated)	White turbidity	White turbidity	Deep brown (precipitated)	Yellowish white turbidity

E_γ was obtained in carbon tetrachloride solution extracted at pH 10.5 and the color reaction (in third column) means the coloration in the water solution when a considerable amount of the element is present.

These results indicated that the reagent is ultimately most sensitive to copper and that interference from other metals is generally negligible even though the acid treatment might not have been the best. If the coloration is produced at pH higher than 10.5, as much as 5 mg. Zn is permissible in 10 γ copper determination as it can be thought $Zn(NH_3)_4$" forms with slightly excess ammonia. Therefore it is possible to determine copper in the presence of a considerable amount of Zn. But in this case, it is safer to make a color comparison immediately as it tends to become turbid on standing. It is easy to prevent the turbidity by lead with the addition of thiourea and in this case the extraction of the copper compound is easily made without the addition of hydroxylamine. Sylvester *et al* reported that 50 p.p.m. each of Co or Ni are permissible with 0.2 to 2.7 p.p.m. copper determination. It is evident from these results that serious interference is far from being encountered, because the amount of these elements in living plants are usually one hundredth to thousandths of the amount of copper.[14]

Likewise it is generally unnecessary to consider the interference of bismuth because of its rarity in biological matter and its lower sensitivity. Thus from the above study of interferences from other metals in copper determination, it can be concluded that the application of this color reaction to copper in biological matter can be successfully undertaken without serious interference.

Hydroxylamine in the extraction The degree of coloration into the aqueous solution is strictly proportional to the amount of copper present, but not when extracted with some organic solvents. It is thought that the rate of transference of colored matter into organic solvents is so small that complete transference is impossible. Thereupon this color reaction has not been widely used though superior in such respects as simplicity, high sensitivity and speed. To overcome these defects Haddok and Evers[8] recommended that extraction be repeated until the solution becomes colorless. Yet this process, it is said by many workers, is not in comformity with the Lambert-Beers' law. Only McFarlane reported that it comforms to the law when extracted with amyl alcohol though the range of concentration proportional to the degree of coloration is somewhat narrow. Nydahl added that this would comform with the law if shaken vigorously about three hundred times for each extraction, but accurate results cannot be expected in this case.

The addition of hydroxlamine in the process of extraction newly tried by the author clearly solves this difficult problem. By its addition in making the extraction with carbon tetrachloride it comforms accurately with the law and brings about the best results by a short

(14) F. Honcamp, "Handbuch der Pflanzenernährung und Düngenlehre", I. 261, Leipzig (1931)

shaking for 20 seconds. The addition of hydroxylamine had been found useful in several cases when tested with solvents which had been proposed. Yet among them carbon tetrachloride is the most advantageous owing to its larger density, lower solubility and lower vapor pressure which are properties convenient for practical use.

and for ineffectiveness on the stability of the coloration. The smaller the pH of the aqueous phase the more necessary is the repetition of the extractive operation.

Though the effective period of the sodium diethyldithiocarbamate solution was reported to be one week or at the most two weeks,[15] it was found that it could be effective for a

Table 2

Stability of the coloration in carbon tetrychloride

	Extinction Coefficient						
Time (min.)	0	30	60	80	100	180	24 hrs.
10.05 γ Cu(a)	0.384	0.380	0.376	0.370	0.373	0.370	0.362
10.05 Cu(b)	0.452	0.436	0.414	—	0.409	0.404	0.401
20.10 Cu(b)	0.755	0.750	—	—	—	0.743	0.735

(a) extracted at pH 10.5 after adding 2 ml. of 4 % hydroxylamine and the final volume, 25 ml.
(b) the same condition as (a) except the addition of 6 ml. of 4 % hydroxylamine.

Another advantage is that it has no ill effect on the stability of the coloration, at the same time preventing any change in coloration.

It was found that no appreciable decrease was noticed after 24 hours standing. Yet the stability decreases slightly upon increasing the amount of hydroxylamine added, though its efficiency for extraction increases. For this therefore 2 ml. of 4 % hydroxylamine solution was found most satisfactory. Further advantage of its addition is found in diminishing the pinkish coloration due to the presence of manganese, if a little excess of ammonia than the recommended is added.

month if used in the presence of hydroxylamine and stored in an amber colored bottle.

Accuracy and reproducibility The addition of hydroxylamine has increased the sensitivity of the reagent as the extraction can be completely carried out. The results obtained on the various concentrations of copper standard solution will be shown in Table 5, indicating that it holds closely to the Lambert-Beers' law therefore rendering the color comparison much more simple.

These results have found that the range of error lies within 5 % according to the amounts of copper (5 γ to 20 γ) in 25 ml. carbon

Table 3

Relation between the amounts of hydroxylamine and the stability of the coloration

4 % hydroxylamine added (ml.)		2	4	6	8
Extinction Coefficient	0 min.	0.384	0.406	0.452	0.509
	30 min.	0.380	0.396	0.436	0.459

Table 4

Efficiency of extraction at various pH (copper present 11.00 γ)

pH	3.0	6.7	7.2	8.6	9.7	10.5	10.9	11.5
Extinction Coefficient	0.430	0.440	0.457	0.451	0.454	0.464	0.434	0.414
Copper found (γ)	10.70	10.95	11.37	11.22	11.29	11.54	10.75	10.30

The extraction must be done under great precaution so that the separated carbon tetrachloride be free from droplets of aqueous solution during the procedure of drawing off from the separatory funnel, which brings about futile oxidation of the reagent in extracted solution. Oxidation of the reagent develops a certain cloudiness.

It was found that pH 7.2 to 10.5 was the the most suitable pH for speedy extraction

tetrachloride solution. But, whenever possible, the copper range selected should not be less than 0.2 p.p.m. in order to obtain greatest accuracy.

In practical use a blank test should be frequently made on all material used. In this case when cells of 50 mm. thickness were used the readings correspond to 0.9 γ copper. When its method is compared with the extractive

(15) J. Grant and A. Mezgy, *Analyst*, **61**, 401 (1936)

Table 5

Accuracy and conformability to the law

Copper present (γ)	Accuracy: Extinction* Coefficient (50 mm. thickness)	Accuracy: Copper found (γ)	Diff. (γ)	Conformability: Extinction Coefficient (average)	Conformability: E_T (Calculated)
2.01	0.081	2.02	+0.01	0.081	0.203
5.03	0.197	4.90	−0.13		
	0.193	4.80	−0.23		
	0.208	5.17	+0.14	0.201	0.201
	0.191	4.75	−0.28		
	0.215	5.35	+0.32		
10.05	0.392	9.83	−0.22		
	0.396	9.95	−0.10		
	0.386	9.60	−0.45	0.401	0.201
	0.401	9.98	−0.07		
	0.408	10.14	+0.09		
	0.422	10.50	+0.45		
20.10	0.820	20.40	+0.30		
	0.800	19.90	−0.20	0.801	0.203

titration or mixed colored method with dithizone,[13] both tedious and requiring skillful operation and a considrable blank factor (owing to the color of the reagent itself), the new method is speedier and more accurate owing to its complete extraction of copper by the addition of hydroxylamine.

Reagent and Apparatus

Apparatus Separatory funnel: Approximately 30 ml. capacity. Silica dish or platinum dish; These apparatus should be free from copper by washing with distilled nitric acid.

Reagent Water; Redistilled in glass apparatus. Hydrochloric acid (1;1): It is preferable to use freshly distilled hydrochloric acid showing constant boiling point. Ammonia saturated: Saturate redistilled water with ammonia gas generating from ammonia aqua on heating by the addition sodium hydroxide. Sodium diethyldithiocarbamate, 0.1 per cent solution; Dissolve 0.5 g. of the reagent in 500 ml. of redistilled water, stored preferably in amber colored bottle. Hydroxylamine, 4 per cent solution; Dissolve 4 g. of its hydrochloride salt in 100 ml. of redistilled water. Carbon tetrachloride: Shake with one tenth of its volume of concentrated sulfuric acid and then wash with redistilled water to remove the latter. After that purify by distillation in usual way.

Procedure

The aliquot portion of the solution containing copper is treated as follows: If copper was concentrated with organic reagent such as dithizone it should be ignited to destroy all organic matter in silica or platinum dish. Then add 1 ml. of hydrochloric acid (1;1) and by means of a glass rod over the interior of the dish so that all the cupric oxide will be dissolved. At this point if copper is less than approximately 10 γ hardly any color is noticeable. Add 10 ml. of water, transfer into the separatory funnel and rinse thoroughly with some water. Thus the solution to be tested is ready for the extraction.

Make the solution alkaline with ammonia to litmus paper and add the excess of 0.2 ml. of ammonia solution. Next add 2 ml. of 4 per cent hydroxylamine solution and 10 ml. of 0.1 per cent sodium diethyldithiocarbamate solution in the order named. It becomes instantly golden yellow due to the copper. Shake vigorously with 7 ml. of carbon tetrachloride and draw it off into a 25 ml. volumetric flask after leaving it to settle. Leave a few drops of the carbon tetrachloride to prevent mixing of the aqueous solution and rinse the stem of the funnel with 2 ml. of carbon tetrachloride. In this extraction the stem should be perfectly dried. Then shake again in the same manner as before. Usually two shakings is sufficient to entirely extract the colord matter. Then fill to the mark with carbon tetrachloride and measure the extinction coefficient with Pulfrich photometer using S 43 filter (434 mμ). If the final volume is reduced to less than 25 ml., then less than 5 γ of copper can be determined with fair results.

Conclusion

The addition of hydroxylamine proposed by the author has removed entirely all defects in the determination of copper with sodium diethyldithiocarbamate as pointed out by previous workers.

Its use has given satisfactory results superior to other methods in the following respects: (a) Speedy and complete extraction of copper diethyldithiocarbamate complex with carbon telrachloride, (b) Normal effect on the stability of coloration and the effective period of the reagent remakably increased and (c) increase of accuracy in color comparison by complete

(13) E.B. Sandell, *Ind. Eng. Chem. Anal. Ed.*, **9**, 464 (1937)

extraction of the colored matter so that it comforms with Lambert-Beers's law.

By the adoption of this method, copper can be determined in a short while after bringing the sample into solution. The experiments already related have proved that it is one of the most accurate methods in comparison with other methods which have been used. At the present time when the role played by copper in biological matter is given greater attention this new method will fulfill its mission in being of invaluable importance in this respect. A new colorimetric method of copper in biological matter adapting both the dithizone extraction and this new method will be reported in the near future by the author.

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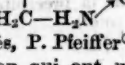
Étude sur la précipitation de la protéine par les sels complexes métalliques II Précipitation de la protéine par les sels complexes du chrome, du fer, de l'argent, et du platine

par Réinosouké Hara

(Reçu le 20 Avril, 1949)

Il existe depuis longtemps beaucoup d'études sur la réaction entre la protéine et le sel inorganique. Certains sels minéraux, comme le phosphotangstate, l'acide hydroferrocyanique, et l'acide métaphosphorique, peuvent précipiter la protéine en solution acide, mais le sel métallique peut la précipiter en solution neutre ou faiblement alcaline. S.E. Michael[1] a classé tous les sels complexes métalliques en deux, complexes cationiques et complexes anioniques, et il a aussi démontré que le sel cationique est capable de précipiter la protéine au domaine plus alcalin que le point isoélectrique et le complexe anionique précipite au domaine acide. Comme les sels complexes du cobalt sont exposés dans mon dernier mémoire,[2] j'ai fait la précipitation de la protéine, et montré que la protéine et le sel complexe peuvent stoichiométriquement réagir, c'est-à-dire, la protéine et le sel complexe forment un composé défini. La protéine est chimiquement un composé qui se combine avec l'acide aminé en donnant un certain type de la liaison, et le corps principal de cette réaction doit être cet acide aminé. H. Ley[3] a déjà donné une formule d'un complexe interne  Cu 1/2 au glycocol-cuivre, et après, P. Pfeiffer[4] a préparé des composés d'addition qui ont une composition défini entre divers sels neutres et des acides aminés comme $LiCl \cdot CH_2{-}NH_2{-}COOH \cdot H_2O$. Il a aussi montré leur constitution X $[H_3N^+{-}COO^-]M^+$, et donne le nom "*amphisalze*" à ces composés. En employant des sels complexes du chrome, du fer, de l'argent, et du platine dans ce précent mémoire, je vais comparer ce résultat au cas des sels complexes cobaltiques déjà publiés dans mon dernier compte-rendu. Les sels complexes utilisés sont des complexes du chrome, et du platine, des complexes cationiques. Des complexes du chrome, du l'argent, et du fer sont encore employés comme des complexes anioniques. Les conditions d'expérience sont identiques aux cas présentés dans le mémoire précedent. Les solutions de tampon employées sont NH_4OH–NH_4Cl à 1/10 N et $(HOOC)_2(CHOH)_2$–$(NaOOC)_2(CHOH)_2$ à 1/10 N, montrent les pH 8.8 et 2.

Détermination de la concentration du sel complexe qui est capable de précipiter la protéine En prenant la solution de la protéine à 0.5%, on les a dissous dans le tampon (pH 8.8 ou 2), ensuite on a ajouté 1 cc. de la solution de diverses concentrations du sel complexe à 1 cc. de chaque solution. On en a examiné les résultats de précipitation après 30 minutes, le résultat est montré dans la table 1 en indiquat "卌" la précipitation parfaite, "卄, +" la précipitation imparfaite, "±" la louche (pas claire) et "−" pas de précipité.

Les complexes cationiques du chrome, du platine ne peuvent pas toujours précipiter la protéine comme ceux du cobalt, tandis que les sels complexes anioniques du chrome, du fer, et de l'argent le font très remarquablement. L'albumine d'oeuf n'est presque jamais pré-

(1) S.E. Michael, *Biochem. J.*, **33**, 924 (1939)
(2) R. Hara, *Cc. Bulletin.*, **22**, 109 (1949)
(3) H. Ley, Ber., **42**, 354 (1909)
(4) P. Pfeiffer et J.V. Modelski, *Z. physiol. chem.*, **81**, 329 (1912), **85**, 1 (1913)

Table 1

sel complexe	caséine	insuline	albumine d'oeuf	gélatine	pH
$[Cr(en)_2Cl_2]Cl\cdot H_2O$ (*cis*)	−	−	−	−	8.8
$[Cr(en)_2(SCN)_2]SCN\cdot 2H_2O$ (*trans*)	−	−	−	−	〃
$[Cr(NH_3)_5SCN](SCN)_2$	+	+	−	−	〃
$[Cr(en)_3]Cl_3\cdot 3H_2O$	++	++	±	−	〃
$[Cr(Co\cdot NH_2\cdot NH_2)_6]Cl_3\cdot 3H_2O$	+++	+++	+++	±	〃
$\left[(en)_2Cr\begin{smallmatrix}OH\\OH\end{smallmatrix}Cr(en)_2\right]Cl_4\cdot 2H_2O$	+++	+++	+	−	〃
$\left[Cr\begin{smallmatrix}OH\\OH\end{smallmatrix}Cr\,en_2\right)_3]Cl_6\cdot 6H_2O$	+++	+++	+	−	〃
$[Pt(NH_3)_4]Cl_2$	−	−	−	−	〃
$[Pt(en)_2]Cl_2$	−	−	−	−	〃
$[Pt(S\cdot C\cdot NH_2\cdot NH_2)_4]Cl_2$	−	−	−	−	〃
$[Pt(NH_3)_2Cl_2]$ ($\alpha\cdot cis$)	−	−	−	−	8.8 et 2
$NH_4[Cr(NH_3)_2(SCN)_4]\cdot H_2O$ (sel Reinécké)	+++	+++	+++	+	2
$K_3[Cr(C_2O_4)_3]\cdot 3H_2O$	+++	+++	+++	+	〃
$K_3[Cr(SCN)_6]\cdot 4H_2O$	+++	+++	+++	+	〃
$(NH_4)_4\left[(C_2O_4)_2Cr\begin{smallmatrix}OH\\OH\end{smallmatrix}Cr(C_2O_4)_2\right]$	+++	+++	+++	+	〃
$K[Ag(CN)_2]$	+++	+++	+++	+	〃
$K_3[Fe(CN)_6]$ (prussiate rouge de potasse)	+++	+++	+++	+	〃
$K_4[Fe(CN)_6]$ (prussiate jaune de potasse)	+++	+++	+++	+	〃

cipitée par les sels complexes cationiques, excepte un complexe d'urée $[Cr(urée)_6]Cl_3$, la gélatine ne l'est guère non plus. Les complexes cationiques du platine ne peuvent pas précipiter même la caséine. Le complexe chromique d'urée peut très remarquablement précipiter la protéine.

a) Précipitation de la protéine par les sels complexes cationiques Les complexes cationique du chrome et du platine ont été utilisés et ces sels, excepte $[Cr(urée)_6]Cl_3$, ne peuvent pas toujours précipiter la protéine, et les complexes du platine employés, ne sont pas capables de précipiter même la caséine et l'insuline. Aucune protéine n'est précipitée par le complexe chromique de la valence +I comme le sel cobaltique, et le sel complexe qui n'a pas de charge électrique tel que $[Pt(NH_3)_2Cl_2]$ ne précipite jamais la protéine, tandis que le complexe d'urée peut considérablement précipiter la protéine. La concentration du complexe cationique qui est nécessaire pour la precipitation est montrée ci-dessous.

b) Précipitation de la protéine par les sels complexes anioniques J'ai employé les complexes du chrome, du fer, et d'argent, qui peuvent parfaitement précipiter la protéine de même que dans le cas du complexe cobaltique.

Table 2

sel complexe	protéine	concentration qui est nécessaire pour la précipitation (mol)	pH
$[Cr(NH_3)_5SCN](SCN)_2$	caséine	1/60	8.8
$[Cr\,en_3]Cl_3\cdot 3H_2O$	〃	1/30 —— 1/300	〃
$[Cr(CO\cdot NH_2\cdot NH_2)_6]Cl_3\cdot 3H_2O$	〃	1/20 —— 1/1000	〃
$\left[en_2Cr\begin{smallmatrix}OH\\OH\end{smallmatrix}Cr\,en_2\right]Cl_4\cdot 2H_2O$	〃	1/100 —— 1/1000	〃
$\left[Cr\begin{smallmatrix}OH\\OH\end{smallmatrix}Cr\,en_2\right)_3]Cl_6\cdot 6H_2O$	〃	1/100 —— 1/3000	〃

Table 3

sel complexe	protéine	concentration qui est nécessaire pour la précipitation (mol)	pH
$NH_4[Cr(NH_3)_2(SCN)_4]\cdot H_2O$	caséine	1/30 — 1/60	2
〃	a'bumine d'oeuf	1/30 — 1/60	〃
$K_3[Cr(C_2O_4)_3]\cdot 3H_2O$	caséine	1/10 — 1/300	〃
〃	albumine d'oeuf	1/10 — 1/350	〃
$K_3[Cr(SCN)_6]\cdot 4H_2O$	caséine	1/10 — 1/300	〃
〃	albumine d'oeuf	1/10 — 1/300	〃
$(NH_4)_4\left[(C_2O_4)_2Cr\begin{matrix}OH\\OH\end{matrix}Cr(C_2O_4)_2\right]$	caséine	1/20 — 1/500	〃
〃	albumine d'oeuf	1/20 — 1/700	〃
$K[Ag(CN)_2]$	caséine	1/20 — 1/100	〃
〃	albumine d'oeuf	1/20 — 1/80	〃
$K_3[Fe(CN)_6]$	caséine	1/10 — 1/300	〃
〃	albumine d'oeuf	1/10 — 1/350	〃
$K_4[Fe(CN)_6]$	caséine	1/10 — 1/600	〃
〃	albumine d'oeuf	1/10 — 1/600	〃

Le domaine de la concentration du sel complexe pour la précipitation est comme suit.

Calcul de l'équivalent de l'ion complexe combiné avec 1 g. de protéine La protéine est précipitée par les complexes, séparée par centrifugation en la lavant cinq fois par l'eau, et on peut sécher dans l'exsiccateur. Le dosage du chrome a été fait comme suit : en prenant 20–30 g de la protéine précipitée, en la décomposant par l'acide azotique fument, en la neutralisant par l'ammoniaque, et en y ajoutant le péroxyde du sodium pour oxyder le sel chromique en chromate, j'ai colorimétriquement fait le dosage du chrome. Pour le dosage du fer, on a traité la protéine précipitée par l'acide azotique fumant, et s'il y a quelque chose d'insoluble, on y ajouté l'acide hydrochlorique, on chauffe au bain-marie pour dissoudre le composé insoluble et on réduit par le chlorure stanneux, puis on peut en faire le titrage par $KMnO_4$ à 1/100N. Pour le dosage de l'argent, en décomposant la protéine précipitée par l'acide azotique fumant, en la diluant avec l'eau et en y ajoutant l'acide hydrochlorique, on peut peser gravimétriquement l'argent comme chlorure. Pour ce dosage du chrome, du fer, et de l'argent, on a d'abord calculé la quantité de l'ion complexe combinée avec 1 g. de protéine, et déterminé l'équivalent de son ion complexe.

a) Equivalents des ions complexes des sels complexes cationiques Les équivalents des ions complexes cationiques sont montrés dans la table 4.

Quant à la caséine, les équivalents des complexes cationiques du chrome présentent généralement des résultats concordants, en indiquant approximativement $90–100\times15^{-5}$, mais les complexes cobaltiques montrent individuellement des valeur assez variables. Mais, la valence +2, comme $[Cr(NH_3)_5SCN](SCN)_2$, m'apparait qu'assez petite. L'équivalent de $[Cr(urée)_6]Cl_3$ donne 63×10^{-5} en albumine d'oeuf qui est plus élevé que dans le cas du complexe cobaltique.

b) Equivalents des ions complexes des sels complexes anioniques Quant aux sels complexes anioniques, leurs équivalents restent constants

Table 4

protéine (solution à 0.5 %)	sel complexe	concentration de la solution du sel complexe (mol)	Cr % dans la protéine précipitée	ion complexe (%)	équivalent de l'ion complexe combiné avec 1g. de la protéine $\times10^{-5}$
caséine	$[Cr(NH_3)_5SCN](SCN)_2$	1/30	1.75 1.64	6.56 6.15	72 67
:	$[Cr\,en_3]Cl_3\cdot 3H_2O$	1/50	1.50 1.38	6.69 6.16	93 85
:	$[Cr(Co\cdot NH_2\cdot NH_2)_6]Cl_3\cdot 3H_2O$	1/50	1.52 1.48	12.04 11.73	100 97
:	$\left[en_2Cr\begin{matrix}OH\\OH\end{matrix}Cr\,en_2\right]Cl_4\cdot 2H_2O$	1/100	2.30 2.27	8.36 8.25	97 95
:	$\left[Cr\begin{matrix}OH\\OH\end{matrix}Cr\,en_2\right)_3]Cl_6\cdot 6H_2O$	1/250	3.12 3.14	10.05 10.11	100 101
albumine d'oeuf	$[Cr(Co\cdot NH_2\cdot NH_2)_6]Cl_3\cdot 3H_2O$	1/20	1.04 0.97	8.24 7.69	65 61

Table 5

protéine (solution à 0.5 %)	sel complexe	concentration de l solution du sel complexe (mol)	Cr,Ag,Fe% dans la protéine précipitée	ion complexe (%)	équivalent de l'ion complexe combiné avec 1g. de la protéine $\times 10^{-5}$
caséine	$NH_4[Cr(NH_3)_2(SCN)_4]\cdot H_2O$	1/20	3.69 3.75	22.57 22.93	91 95
〃	$K_3[Cr(C_2O_4)_3]\cdot 3H_2O$	1/40	1.48 1.40	8.99 8.51	94 88
〃	$K_3[Cr(SCN)_6]\cdot 4H_2O$	1/40	1.47 1.50	11.31 11.54	96 98
〃	$(NH_4)_4\left[(C_2O_4)_2Cr\langle^{OH}_{OH}\rangle Cr(C_2O_4)_2\right]$	1/80	2.31 2.27	10.88 10.70	100 98
〃	$K[Ag(CN)_2]$	1/20	7.74 8.00	11.47 11.85	81 84
〃	$K_3[Fe(CN)_6]$	1/40	1.61 1.75	6.10 6.62	92 105
〃	$K_4[Fe(CN)_6]$	1/80	1.27 1.18	4.81 4.47	96 88
albumine d'oeuf	$NH_4[Cr(NH_3)_2(SCN)_4]\cdot H_2O$	1/20	2.98 2.71	18.22 16.58	70 63
〃	$K_3[Cr(C_2O_4)_3]\cdot 3H_2O$	1/40	1.23 1.18	7.47 7.17	77 73
〃	$K_3[Cr(SCN)_6]\cdot 4H_2O$	1/40	1.14 1.10	8.77 8.46	72 69
〃	$(NH_4)_4\left[(C_2O_4)_2Cr\langle^{OH}_{OH}\rangle Cr(C_2O_4)_2\right]$	1/80	1.90 1.84	8.95 8.67	80 77
〃	$K[Ag(CN)_2]$	1/20	6.25 5.78	9.26 8.56	64 59
〃	$K_3[Fe(CN_6]$	1/40	1.25 1.18	4.73 4.47	70 66
〃	$K_4[Fe(CN_6]$	1/80	1.10 1.04	4.16 3.94	82 77

indépendamment de l'espèce et de la valence des complexes, et s'accordent suffisamment avec les valeurs données par les complexes anioniques du cobalt. Les équivalents des complexes anioniques ont montré ci-dessous.

Conclusion (1) La précipiation de la protéine par les sels complexes cationiques du chrome est imparfaite comme ceux du cobalt, tandis que les complexes anioniques du chrome, du fer, et de l'argent donnent une précipitation parfaite.

(2) Les complexes cationiques du chrome ne peuvent pas toujours précipiter la protéine, et ceux de la valence +1 ne peuvent jamais précipiter aucune protéine.

(3) Les complexes cationiques du platine ne peuvent pas non plus précipiter la protéine.

(4) Le sel complexe qui n'a pas de charge électrique, tel que $[Pt(NH_3)_2Cl_2]$ ne peut jamais précipiter la protéine.

(5) Le complexe d'urée de chrome montre une grande capacité de précipitation sur la protéine, mais on ne comprend pas si ce caractère doit sa forme à la liaison dans son radical complexe.

(6) Les équivalents calculés de la quantité du métal dans la protéine précipitée ne sont pas déterminés au cas des complexes cationiques du chrome à cause de la précipitation imparfaite, mais, cette variation est moindre que celle montrée par le complexe cobaltique.

(7) Les équivalents des sels complexes anioniques du chrome, du fer, et de l'argent ne sont pas différents les uns des autres, s'accordant suffisamment avec le cas du cobalt, et en générale ils restent constants, indépendamment de l'espèce et la valence des complexes.

(8) L'équivalent du complexe d'urée du chrome par rapport à l'albumine d'oeuf est plus élève que celui donné par le complexe cobaltique.

(9) De ces résultats obtenus, on peut conclure que la protéine et le sel complexe réagissent stoichiométriquement, et les sels complexes cationtiques du chrome, à l'exception de complexe d'urée du chrome, ne donnent pas de précipitation parfaite en ne montrant pas l'équivalent maximum de l'ion complexe combiné avec 1g de protéine. On peut cependant obtenir la précipitation parfaite et l'équivalent maximum par les complexes anioniques du chrome, du fer, et de l'argent. Le complexe d'urée du chrome est aussi parfaitement capable de précipiter la protéine et montré son équivalent maximum.

Les présentes recherches ont été menées à bien grâce à l'aimable indication de M. le

Prof. Kénjiro Kimura. Je tiens aussi à exprimer ma vive reconnaissance à M. M. les Prof. Toshi Inoué, Taku Uémura et Eiji Ochiai qui ont bien voulu me donner de très utiles conseils pour mes études.

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A New Method of the Graphical Representation of a Quarternary System on a Plane Surface*

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Introduction To represent the phase equilibrium of a quartenary system under constant temperature and pressure, a regular tetrahedron or generally a three-dimensional space figure may be employed. When such a model is considered to be placed on a plane which intersects with the three axes at equal angles, it forms, so to speak, a pyramid with three faces. For the representation of the system on a plane surface, the projection of the model on the base of the pyramid has been employed usually. The projection is orthogonal (perpendicular), or clinographical (perspective) from the zenith of the pyramid.[1][2] However, to express the three coordinates of a space figure on a plane surface, one projection is obviously insufficient, and a numerical table or an additional figure is necessary to supplement it. Moreover, for the representation of these projections, a triangular section-paper must be used and, consequently, the treatment of the figure is rather troublesome.

Since the phase rule of a quarternary system is particularly important to treat sea water systematically*** or to establish the sea-salt industry,[3] a convenient new method of representing the system on a plane surface will be proposed in the present report, and, by the use of this method, the crystallization processes in the system will be solved quite generally.

New Method Proposed. The method of the graphical representation proposed here is, as shown in Fig. 1, to project the three-dimensional space model of the system, axes of which intersect each other at right angles, orthogonally on two of the axual planes (i.e., on the surfaces of the pyramid). The two projections correspond to the plan and the elevation of the model. The composition of the system will be expressed, as usual, in terms of the absolute number of equivalents of the solutes per 1000 mols of the solvent.* Fig. 1

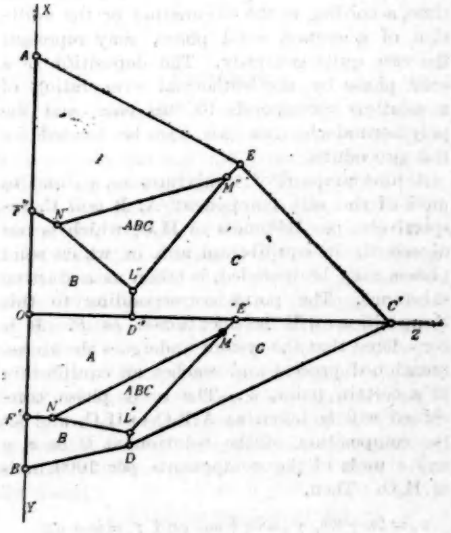

Fig. 1

is the projection of an ideal system, with three salt components and water, on the axual planes *YOZ* and *XOZ*. There exist four solid

* Phase-rule Studies on the Sea-Salt Industry. I. Presented at the meeting of the Kinki-Section of the Chemical Society of Japan at Kyoto on May 7, 1949.

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*** A comprehensive review of the literature on the equilibria of the system of sea-salts has been made by D'Ans in (1). While main salt components of sea water are chlorides and sulphates of sodium, potassium and magnesium, owing to the predominance of NaCl, deposition of the other salts takes place always in the coexistence of it; and, under these circumstances, the system can be treated as a quarternary system consisting of three salts or radicals, and water.

(1) J. D'Ans, "Die Lösungsgleichgewichte der Systeme der Salze ozeanischer Salzablangerungen," Berlin (1933)

(2) W. C. Blasdale, "Equilibria in Saturated Salt Solutions," New York (1927)

(3) *Cf.*, Y. Tanaka, *J. Japanese Chemistry* (*Kagaku-no-Ryoiki*), **3**, 224 (1949)

* For the system of sea-salts, it is convenient to take K_2^{++}, Mg^{++} and SO_4^{--} as unite equivalents.

phases **A**, **B**, **C** and **ABC** in this example.*

The two projections of the present figure represent the isothermal of the system completely. The three coordinates of a point can be known immediately from the figure; and, as the coordination is rectangular, the drawing and reading of the figure are very easy by the use of common section-paper. As will be shown later, the graphical solution of the crystallization processes can be executed quite conveniently. Only it is advisable to select the planes of projection according to the system or to the object of the study. Reciprocal salt pairs can also be expressed completely by the present figure. Two cations and one anion or the converse are taken as the salt components, a part of the space being left without use.

Mathematical Solution of the Crystallization Processes Such cases as only a single solid phase is concerned are not yet completely discussed in the four-component system consisting of three salts and water, while the deposition of two or three solid phases at the same time has already been treated extensively. Therefore, before treating the crystallization processes graphically, general solution of the above problem will be made.

An isothermal process, in which the compositon of the solution changes according to the water content of the system due to the concentration or the dilution and, at the same time, according to the elimination or the addition of a certain solid phase, may represent the case quite generally. The deposition of a solid phase by the isothermal evaporation of a solution corresponds to this case, and the polythermal changes can also be treated by this procedure.

A unit amount of a mixture, x_p, y_p and z_p mols of the salt component A, B and C, respectively, per 1000mols of H_2O, which is not necessarily in equilibrium and in which solid phases may be included, is taken as a starting substance. The point corresponding to this composition will be mentioned as P. It is considered that the system undergoes the abovementioned process and reaches an equilibrium at a certain point, Q. The solid phase concerned will be taken as $A_hB_iC_j \cdot mH_2O$, and let the composition of the solution at Q be x, y and z mols of the components per 1000 mols of H_2O. Then,

$$x_p = hn + wx,\ y_p = in + wy \text{ and } z_p = jn + wz \quad \ldots\ldots\ldots (1)$$

where $1000w$ is the water content in mol of the solution of Q, and n is the amount of the compound substracted from the system in mol up to that time.* Since, in the present process, the composition of the solution may be altered from the point P along this plane, the plane will be mentioned as the composition plane.

Now, when the solid phase exists at Q, as the system is considered to be in equilibrium, Q should lie at the same time on the saturation surface of the compound. Therefore, Q is to lie on the intersecting line between the composition plane and the saturation surface, and, if they do not cross each other practically, the compound does not appear as a solid phase. This line is the crystallization path from P with regard to the solid phase in question.

Generally, the saturation surface of a compound is by no means plane. However, when it is assumed as such, a point on this plane can be expressed as

$$x/a + y/b + z/c = 1 \quad \ldots\ldots\ldots (2)$$

where a, b and c are the length of the three axes OX, OY and OZ at which they intersect with the saturation plane.** Then the crystallization path in question can be obtained from (1) and (2) as a straight line. Thus the path has been determined mathematically quite in general. When a third condition is defined, special points on the path can also be determined.

Application of the New Method on the Graphical Solution Now, the above mentioned process will be followed graphically by using the present figure. At first, the intersection of a plane saturation surface (or generally a plane) with the plane of projection will be considered. The trace of the saturation surface of the compound **ABC** in Fig. 1, LMN, on the plane XOZ will be taken for illustration. As shown in Fig. 2, let the line MN cross with XOZ at t, and t' be its projection on YOZ. Then, since t' should lie on OZ, the point can be found from the figure at once, and consequently, t is easily obtainable. The same is for w' and w, and the trace can be represented by the line tw. Similarly, LMN intersects with YOZ on uv, and accordingly, the intersecting points of this plane with the axes OX, OY and OZ (a, b and c) are determined immediately.

The determination of the trace of a composition plane on the axual planes is more simple. For example, the trace of this plane on XOZ is expressed, from (1), as

* The figure has been chosen so that all the saturation surfaces are plane.

* According to the concentration or the dilution, $w<1$ or >1; and since $n>0$ by the elimination, $n<0$ by the addition. As h, i and j are simple intergers and frequently some of them become 0, the equations are simplified for practical instances.

** According to the orientation of the plane, a, b and c may have negative values.

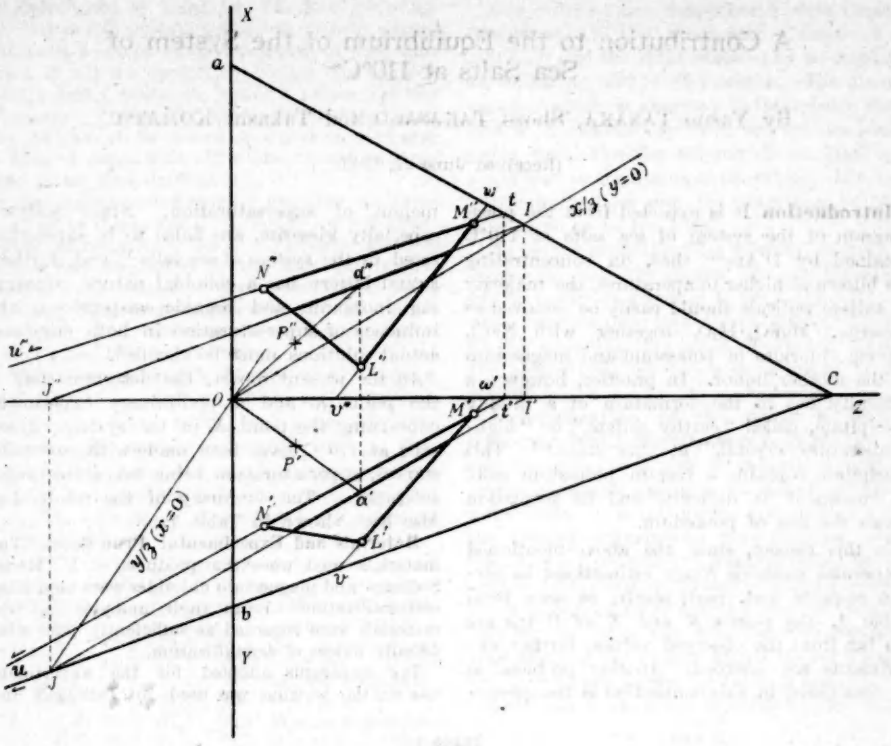

Fig. 2.

$$x/z=(jx_p-hz_p)/(iz_p-jy_p),$$

because $y=0$ on this plane. For the compound **ABC**, as $h=i=j=1$, it becomes

$$x/z=(x_p-y_p)/(z_p-y_p).$$

The line is shown in Fig. 2, and it crosses with ac at I, and similarly the trace on YOZ crosses with bc at J. Then, IJ represents the intersecting line between the saturation plane and the composition plane; it is the crystallization path. In the figure, the path is shown as its projections, IJ'' and $I'J$.

Curved saturation surfaces may be treated by assuming that a limited part of them is plane. Special points on the path can also be obtained easily, and the behavior of crystallization on the boundary of the saturation surface has, as already mentioned, been discussed extensively. The present method may particularly be suitable for the treatment of these instances.* The details will be published elsewhere.

Summary

A new method of representing the phase equilibrium of a quarternary system under a constant temperature and pressure on a plane surface has been proposed. The method is to project the three-dimensional space model of the system, axes of which intersect each other at right angles, orthogonally on two of the axual planes. The two projections can represent the complete state of the system, and the treatment of the figure is quite simple and convenient.

The crystallization processes in such a quarternary system have been solved mathematically quite in general, and the application of the present method of graphical representation on the solution of the processes has been illustrated.

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* For instance, on concentrating the solution with the composition at P, **A** begins to deposit at α in Fig. 2.

A Contribution to the Equilibrium of the System of Sea Salts at 110°C*

By Yasuo TANAKA, Shozo TAKASAGO and Takashi KOMATSU

(Received June 21, 1949)

Introduction It is expected from the phase diagram of the system of sea salts at 110°C obtained by D'Ans[1] that, on concentrating the bittern at higher temperatures, the majority of sulfate radicals should easily be removed as kieserite, $MgSO_4 \cdot H_2O$, together with NaCl, leaving chlorides of potassium and magnesium in the mother liquor. In practice, however, a difficulty lies in the formation of a muddy precipitate, called "earthy sulfate" or "high-temperature crystal," at this stage.[2] This precipitate contains a certain potassium salt; its treatment is difficult, and its formation causes the loss of potassium.

In this respect, since the above-mentioned isothermal contains rough estimations in certain respects and, particularly, as seen from Table 1, the points K and X of D'Ans are too far from the observed values, further experiments are desirous. Another problem to be considered in this connection is the phenomenon of supersaturation. Since sulfates, especially kieserite, are liable to be supersaturated in the system of sea salts[3] and, further, actual bittern has a colloidal nature, containing inorganic and organic suspensions, the influence of supersaturation in both pure and actual solutions must be clarified.

In the present report, the determination of the point K and a preliminary experiment concerning the point X in the system of sea salts at 110°C have been made with pure substances, supersaturation being taken into consideration. The summary of the results has also been shown in Table 1.

Materials and Experimental Procedure. The materials used were the products of E. Merk. Sodium- and magnesium chlorides were used after recrystallization. From their analyses, all the materials were regarded as sufficiently pure with definite waters of crystallization.

The apparatus adopted for the experiment was similar to what was used by Tschugäff and

Table 1

Pt*	Literature	Temp. (°C)	Na_2Cl_2 (mol/1000 mol H_2O)	K_2Cl_2	$MgCl_2$	$MgSO_4$	Solid phases
I	Leimbach[4]	100	16	—	26	10	NaCl, Vant., Löw.
	D'Ans[1]	110	34	—	27	11	
I, K	D'Ans[1]	111	33.5	—	27.5	10.5	Löw.+Vant.→Kies. (+NaCl)
K	Leimbach[4]	100	16	—	49	11	NaCl, Löw., Kies.
	Maeda[5]	105	21.298	—	44.08	11.32	
	D'Ans[1]	110	33.0	—	28	11	
	Tanaka	〃	17.5	—	49.5	13.5	
X	Leimbach[4]	105	26.8	9.1	31.45	11.86	NaCl, Löw., Kies., Lang.
	Tanaka	110	20	12	41	8	Löw.+Vant.→Kies.
X, Y***	D'Ans[1]	108	26.5	29.6	14.0	16.0	(+Lang.+NaCl)
Y	〃	110	26.1	30.2	14.3	15.7	NaCl, Vant., Löw., Lang.

* Notions are followed after D'Ans. However, the point Y of him is denoted here as X, because the point has been expressed him by as X below 83°. Below 83°, X is the coexisting point of NaCl, kieserite, langbeinite and kainite.

** The values of D'Ans are estimated, and the others are observed ones.

*** According to the diagram of D'Ans, since this transition takes place at 103°, löweite does no more coexist with langbeinite at 110°. A new bivariant point, NaCl, Vant., Kies. and Löw., must be given at this temperature, although the point is abridged in his diagram.

* Phase-Rule Studies on the Sea-Salt Industry. II. Presented at the meeting of the Kinki-Section of the Chemical Society of Japan at Kyoto on May 7, 1949.

(1) J. D'Ans, "Die Lösungsgleichgewichte der Systeme der Salze ozeanischer Salzablagerungen," Berlin (1933)

(2) Cf., T. Nishimura, *J. Soc. Chem. Ind. Japan.* **20.** 384, 587 (1917); **22.** 255 (1919); S. Oka, *J. Electrochem. (Japan)*, **11,** 186 (1943)

(3) Cf., for instance, H.L. Robson, *J. Am. Chem. Soc.*, **49,** 2772 (1927); V.G. Kuznetsow, *Bull. acad. sci., U.R.S.S., Classe sci. math. nat., Ser. Chim.* **1937,** 385

(4) G. Leimbach, *Mitt. K.F.A*, **4.** 11 (1925); G. Leimbach and A.Pfeiffenberger, *Caliche*, **11,** 428(1930)

(5) T. Maeda, *J. Soc. Chem. Ind., Japan*, **23,** 573, 954 (1920). It is regrettable Maeda's research is neglected by D'Ans. D'Ans seems to have extrapolated these two points chiefly from the data at lower temperatures.

Chlopin[6] and by Maeda.[5] The principle of the method is to maintain the system without evaporation at constant temperature and, at the same time, to stir the system by boiling the solution with a reflux condenser under a proper reduced pressure.* Portions of the solution were taken out for analysis by means of a pipette fitted with a filter of cotton wool. The determinations of the solid phase were omitted.

The analyses were carried out after the usual analysis of the pittern.[7] Chloride ion was determined volumetrically by the Vorhard's method, sulfate and magnesium by the usual gravimetric methods and potassium gravimetrically as $NaK_2Co(NO_2)_6 \cdot H_2O$. Sodium was estimated by the difference.** The results were expressed as mols of radicals per 1000 mols of water.

The System, $MgCl_2$-$MgSO_4$-H_2O To know the general conception of the crystallization velocity of kieserite at higher temperatures, this two-salt system was studied at first. The experiments were carried out under various conditions, and the solutions were analysed from time to time. The results are arranged in Table 2.

Table 2

Expt. No.	Time (hr.)	Mg (mol/1000 mol H_2O)	Cl_2 (mol/1000 mol H_2O)	SO_4 (mol/1000 mol H_2O)	Initial conditions and remarks
1	5	86.2	73.5	12.6	No precitate at
	7.5	83.5	73.7	9.8	room temp. It was
	12.5	81.9	74.7	7.2	formed after heat-
	15	81.6	74.6	7.0	ing 3.5 hrs.
2	2.5	74.5	65.9	8.6	With some precipi-
	4.5	75.7	67.3	7.3$_5$	tate at room temp.
	6	75.6	68.2	7.3$_5$	(The sample in 1 was used after dilution.)
3	1	125.4	121.7	3.6$_5$	An excess of $MgSO_4$
	2	125.8	122.1	3.7	was presented at
	4	125.9	122.3	3.6	room temp.
4	2	84.9	73.8	11.1	With a slight pre-
	4	83.4	74.4	9.0	cipitate at room
	6	84.4	75.9	8.5	temp.
5	1	113.1	107.3	5.8	The solution was
	2	116.6	111.1	5.5	concentrated by
	4	119.1	115.0	4.1	boiling, and the
	6	120.6	116.7	3.9	measurement was commenced after some precip. was observed.
6	2	70.4	58.3	12.1	As in 5.
	4	68.4	57.9	10.5	
	6	69.2	58.9	10.3	
7	2	84.5	73.9	10.6	Some $MgSO_4 \cdot 7H_2O$
	4	83.1	73.5	9.6	was added at high
	6	83.2	74.4	8.8	temp. It was once dissolved, and the precip. was observed again after 0.5 hr.

Our results agree rather better with those of Maeda at 105°C[5] than with Campbell's at 100°C,[8] and the solid phase may be regarded as consisting always of kieserite. The discontinuity, which is observed in Campbell's result and is considered by him as the transition point from kieserite to anhydrous $MgSO_4$, is never seen in the results of the others. His data, particularly those near the transition point of him, seem to be too high.

As for the crystallization velocity, it may be concluded from the results that the formation of the nuclei of kieserite is very difficult, and, when they are once formed to a certain amount, further crystallization takes place smoothly and the system reaches to an equilibrium within several hours.

Determination of the point K in the System, NaCl-$MgSO_4$-$MgCl_2$-H_2O As the general tendency of the crystallization velocity in the system of sea salts at higher temperatures could be seen from the above experiment, the present experiments were executed under the following procedure: a mixture with a certain composition, nearly saturated or with a precipitate, was concentrated step by step by boiling, and for each step the solution was analysed after keeping the system at 110°C for 5 hours. The results are shown in Table 3 and Fig. 1.* Considering from the composition of the start-

Table 3

Expt. Ser.	No.	Na_2 (mol/1000 mol H_2O)	Mg (mol/1000 mol H_2O)	Cl_2 (mol/1000 mol H_2O)	SO_4 (mol/1000 mol H_2O)	Total salts	Solid phases
A	—	(25	50	60	15	75)	(initial composition)
	11	23.3	54.3	64.9	12.7	77.6	NaCl, Löw.
	12	20.5	58.5	65.9	13.1	79.0	〃 〃
	13	15.4	66.3	68.2	13.5	81.7	〃 〃 (metastable)
	14	10.9	73.0	70.1	13.8	83.9	〃 〃 (metastable)
	15	11.7	68.0	69.5	10.2	79.7	NaCl, Löw., Kies. (not in equil.)
B	—	(14	54	35	33	68)	(initial composition)
	16	9.4	70.2	54.4	25.2	79.6	Löw., Kies.
	17	15.1	64.9	62.9	17.1	80.0	〃 〃
	18	19.3	60.9	71.1	9.6$_5$	80.2	〃 〃 (metastable)
C	—	(16	53	53	16	69)	(initial composition)
	19	16.7	62.9	65.8	13.7$_5$	79.6	Löw. (near K-point)
	20	14.7	64.5	71.6	7.6	79.2	NaCl, Kies
	21	11.8	69.3	75.5	5.6	81.1	〃 〃
D	22	9.7	75.0	79.2	5.5	84.7	NaCl, Kies.
	23	5.2	87.4	89.5	3.1	92.6	〃 〃
	24	0.4	109.0	107.1	2.3	109.4	〃 〃
	25	0.1	119.0	117.4	1.7	119.1	〃 〃

* In the present case, as the solutions boil at 110° under a pressure not so far from 1 atm., the effect of pressure on the solubility may be neglected.

** In the case of the partial system, $MgCl_2$–$MgSO_4$–H_2O, magnesium was also estimated by the difference, because its direct determination was not so accurate when it existed in large quantities.

(6) L.A. Tschugäff and W. Chlopin, *Z. anorg. Chem.* **86**, 154 (1914)

(7) Cf., N. Naito and T. Mizuno, "Method of Inorganic Analyses and Tests," Dairen (1944)

* As for the graphical representation of the system used here, see I of this report (this Bulletin, **23**, 11 (1950)

(8) A.N. Campbell, K.W. Downes and C.S. Samis, *J. Am. Chem. Soc.*, **56**, 2507 (1934)

ing mixtures, these solutions are well explained as being in contact with the solid phases described in the table, respectively.

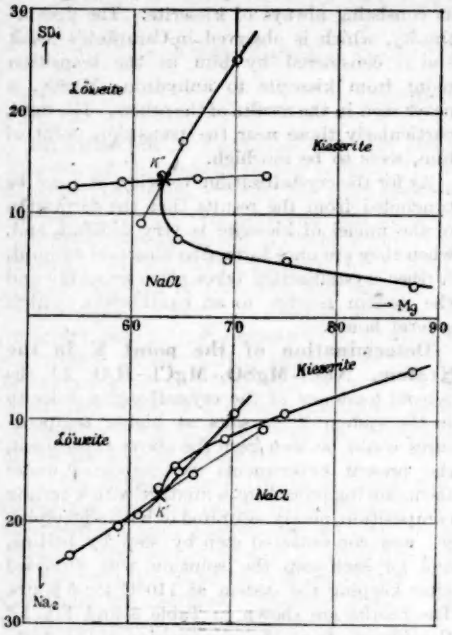

Fig. 1

In the figure, three boundary curves cross each other quite well at one point, and so it can be regarded as the point K. The fact that the curves of series A and B extend beyond this point may be explained as due to the existence of meta-stable equilibrium owing to the difficulty of transformation of the crystals once deposited, or to the phenomenon of supersaturation. The composion of the point is near to

Na_2 17.5, Mg 63, Cl_2 67 and SO_4 13.5

mols per 1000 mols of H_2O.

To compare the result with the data in Table 1, our result coincides quite well with that of Leimbach at 100°C. Maeda's result at 105°C also lies not so far from them. The magnesium content of the point by D'Ans is obviously too small. Consequently, the point K of D'Ans at 110°C should be revised, and löweite should have a considerably larger field of existence at higher tempetatures.

Preliminary Experiment on the System, NaCl-KCl-$MgSO_4$-$MgCl_2$-H_2O The solubility determinations in the five component system of sea salts, particularly those of the boundary curve between the points X and R at 110°C have been undertaken. Although the experiment is not yet completed, it is concluded at least that the potassium contents of the results are smaller and the magnesium contents are larger, particularly in the vicinity of the point X, than what are expected from the diagram of D'Ans. The point X seems to lie at about

Na_2 20, K_2 12, Mg 49, Cl_2 73 and SO_4 8

mols per 1000 mols of H_2O, and the point agrees pretty well with that of Leimbach at 105°C (cf., Table 1). The point X of D'Ans, too, seems to be revised, and langbeinite may have a larger field.

However, even if the point X lies where it is found in the present result, the crystallization path in concentrating sea water at higher temperatures is to pass through the kieserite field as well, and there is no possibility of depositing langbeinite or other salts on the way. Extensive studies in this concern is desirous, and, at the same time, supersaturation in the actual evaporation of the bittern must be examined carefully.

Summary

1. The solubility of magnesium sulfate in magnesium chloride solution at 110°C has been studied with a special reference to the crystallization velocity. In this system, it seems that the formation of the nuclei of kieserite is very difficult, and, when they are once formed, further crystallization takes place smoothly.

2. In the system, NaCl-$MgSO_4$-$MgCl_2$-H_2O, at 110°C, it has been found that the point K lies at about

Na_2 17.5, Mg 63, Cl_2 67 and SO_4 13.5

mols per 1000 mols of H_2O. The content of magnesium is much larger than what has been estimated by D'Ans, and, accordingly, the löweite field of him should be enlarged.

3. Preliminary experiment on the five component system of sea salts at 110°C has shown that langbeinite may have a larger field than expected from the diagram of D'Ans.

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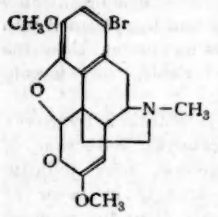
On the Reduction of 1-Bromo-sinomeneine*

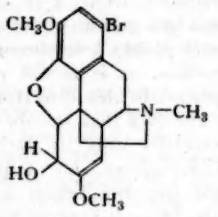
By Kakuji Goto, Tatsuo Arai and Tetsuro Kono

(Received July 16, 1949)

By the catalytic reduction of 1-bromo-sinomeneine (I) in weakly acidic solution, as well as by the sodium-amalgam reduction, its oxide ring is invariably opened and we obtain a mixture of alkali-soluble bases, which is almost inseparable into pure components. However, by the reduction with aluminium isopropylate we obtained a base of m. p. 171°C, to which we give the constitution II and which we will call 1-bromo-sinomeneine-alcohol from the following reasons:



I



II

(1) The base of m. p. 171°C is insoluble in 2% caustic soda and gives no ferric chloride reaction.

(2) By benzoylation, it gives a monobenzoyl derivative, but it is not reacted by diazomethane.

(3) It contains two original methoxyl groups, one of which is exceedingly hydrolysable with dilute acid (enol methoxyl).

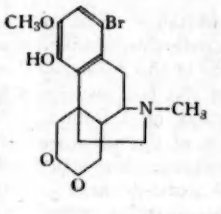
(4) It gives 1-bromo-diacetyl-sinomenol, namely, 1-bromo-3, 7-dimethoxy-4, 6-diacetoxy-phenanthrene, on acetolysis.

The substance of m. p. 171° may be, therefore, an optical antipode of hypothetical 1-bromo-7-methoxy-codeine, for it contains the morphine skeleton and all its functional groups, but superfluous bromine and enol-methoxyl at the same time.

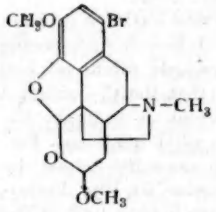
A very remarkable property of this substance is the ease, with which it is converted into 1-bromo-sinomeninone (III). For instance, when the substance of m. p. 171° was dissolved in 2% hydrochloric acid at room temperature and when the solution was immediately made alkaline with sodium carbonate, we obtained 1-bromo-sinomeninone in 64% yield. It seems that the mere dissolution of the substance in a dilute mineral acid effects this deep-seated transformation.

Now, we find several cases of hydrolytical opening of oxide-ring in the chemistry of the morphine group as in the molecular rearrangement of thebaine into thebenine or of morphine into apomorphine. In both cases, a stronger acid (14% or fuming) and a higher temperature (100° or 130°) are necessary. Only in the conversion of β-chlorcodide into β-ethyl-thiocodide, the opening of oxide-ring is effected by 5/2 N caustic soda at the boiling temperature (after Small).

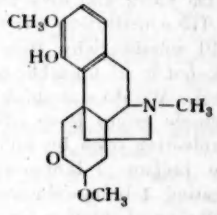
The above-mentioned property of this substance led us to some confusion at the earlier stage of investigation. We supposed at first the substance of m. p. 171° had the constitution IV, namely 1-bromo-dihydrosinomeneine, on the ground that the substance of this constitution could never be obtained by the bromination of



III



IV (hypothetical)



V

dihydrosinomenine (V), but we always got 1-bromo-sinomeninone (III) instead.[1] We suspected that this might have been due to the easy decomposition of preformed IV into the more stable III.

If it is the case, then the substance of m. p. 171° formed by the reduction, may be decomposed into III by a slight shock, namely by the dilute hydrochloric acid. It may be strange that the ketonic group remains intact, while the double linkage is reduced by Meerwein-Pondorf's method. But Lund[2] gives an instance where ketonic group and α, β-double bond were reduced simultaneously.

In this respect, we applied the above reduction method to sinomenine and 1-bromo-sinomenine, with the results that both these substances were very difficultly reduced on their ketonic group. We recovered some unchanged

* Studies on Sinomenine, Part LXII. Parts LIX and LX, Acta Phytochimica. XV, 183, 187 (1949)

(1) *Ann.*, **489**, 94 (1931)
(2) **Ber.**, **70**, 1520 (1937)

substances, but could not isolate reduced bases in crystalline state.

Catalytic reduction of 1-bromo-sinomeneine in pyridine solution, using PtO_2 as catalyst, was more fruitful. It gave the substance of m. p. 171° and 1-bromo-dihydrosinomenine, each in a 10-20% yield. This indicates that in some molecules the ketonic group only and in others the double bond as well as the oxide-ring are reduced. However, in sinomenine and 1-bromo-sinomenine the reduction goes on in a somewhat different way. For, we obtained from the former dihydrosinomenine and dihydrosinomeninol, and from the latter, 1-bromo-dihydrosinomenine. Thus the oxide-ring seems to play an important part in the catalytic reduction as well as in the Meerwein-Pondorf's reduction.

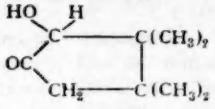
The production of the substance of m. p. 171° in the above catalytic reduction seems to have decided the constitution of this substance in favor of formula II. But the last decision was given by the reformation of 1-bromo-sinomeneine by the oxidation of the substance of m. p. 171° by Pshorr's method. The latter gave on the oxidation with chromic acid as well as with potassium permanganate, the starting material, 1-bromo-sinomeneine, in tolerable yield, viz. 40% resp. 20%.

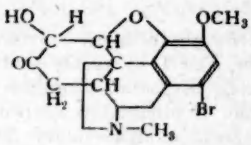
The constitution being thus settled, a problem still remains, why then 1-bromo-sinomeneine alcohol is so unstable towards dilute mineral acid. We do not think that the $C_{(7)}$-situated ketonic group is so efficient as to make the oxide-ring open by such mild treatment. For, we prepare 1-bromo-sinomeneine-ketone by heating 1-bromo-sinomeneine in 10% hydrochloric acid solution for one hour at 100°.[3] The fission of oxide-ring may be, therefore, brought about perhaps by one of the following causes.

(1) The $C_{(6)}$-situated alcohol group may cooperate with $C_{(7)}$-situated ketonic group to open the oxide-ring. The newly introduced alcoholic group may converge to one ketonic group in $C_{(6)}$ to be able to conjugate the ketonic group in $C_{(7)}$. The drawback of this supposition is that we have no similarly constituted morphine alkaloids, and therefore have met with no analogical transformation.

(2) The second theory is based on α-ketol-rearrangement and recurs to the above hypothetical 1-bromo-dihydrosinomeneine (IV). If the $C_{(6)}$-alcoholic and $C_{(7)}$-ketonic group, produced by the hydrolysis of the enol methoxyl, interchanged the position by α-ketol-rearrangement, then the supposed very unstable base IV might be produced, and this may be instantly transformed into 1-bromo-sinomeninone, owing to its supposed unstability.

This transformation, caused by such mild reagent, might at first seem very strange, but the investigation of Ingold and Shoppee[4] on the tautomerism of 1-hydroxy-2, 2, 3, 3-tetramethyl-cyclopentanone-5 seems to throw some light on the above view.





Naturally, there may be some deep difference in the behaviour of 5-membered and 6-membered rings, yet the similarity of the constitution of these two substance is more than apparent. If, by the α-ketol rearrangement, the $C_{(6)}$-ketonic and $C_{(7)}$-alcoholic base is produced from 1-bromo-sinomeneine-alcohol even in a minute quantity and transformed into more stable 1-bromo-sinomeninone, then the reaction, as it is not reversible, may largely proceed in this direction.

The fact that we always obtain 7-hydroxy-derivative only in the catalytic reduction of sinomeninone, an α-diketone, may indicate that the equilibrium is strongly in favor of 7-hydroxy-6-keto-derivative than the reversed one.

Experimental

(1) Preparation of 1-bromo-sinomeneine alcohol

A. With aluminium isopropylate The apparatus was constructed after H. Lund.[2] One and half gram of aluminium-isopropylate was dissolved in 20 cc. isopropyl alcohol and 2g. of 1-bromo-sinomeneine was added. The reduction was carried out on a steam bath and was complete after two or three hours, during which 50 cc. isopropyl alcohol were added in drops. Then the solvent was distilled over and the residue was treated with 11% cold caustic soda solution so as to dissolve the aluminium hydroxide almost completely. The alkaline solution was then shaken with ether four times. When the dried ether was distilled away, 1-bromo-sinomeneine alcohol crystallized out in stout prisms. The crystallisation can be accelerated with addition of alcohol. M. p. 171°. Yield 40-60%. Recrystallization from methanol, alcohol or acetone did not raise the melting point. The substance showed no coloring with ferric chloride in methanol solution.

Analysis Found: C, 56.17; H, 5.422; N, 3.374; CH_3O, 14.93%. Calc. for $C_{19}H_{22}O_4NBr$ (408): C, 55.88; H, 5.39; N, 3.431; CH_3O, 15.20%. Sp. rotation. 0.2055g. subst. was dissolved into 10 c.c. methanol.

$\alpha = +1.10°$ $[\alpha]_D^{19} = 1.10/2.055 \times 100 = +53.530°$.

Mol. weight after Rast. Camphor, 3.274, 3.834, 3.460 mg.; subst., 0.195, 0.336, 0.358 mg. $\Delta = 6.0°$, 8.5°, 10.6°

Mol. weight = 379, 412, 390

(3) This Bulletin, **5**, 165 (1930)

(4) Shoppee, *J. Chem. Soc.*, **1928**, 1667

Methiodide Prepared in methanol solution and recrystallized from water. M. p. 232-233° Analysis. Found; C, 43.52; H, 4.504; I, 23.01%. Calc. for $C_{20}H_{25}O_4NBrI$: C, 43.64; H, 4.54; I, 23.08%

Once, when the methanol solution was boiled, we obtained the methiodide of 1-bromo-sinomeninone (m. p. 245-246°), instead of that of the original substance. This might be due to the liberation of hydroiodic acid during the reaction. (compare (2))

Monobenzoylester 0.5g. of 1-bromo-sinomeneine alcohol was dissolved in 1 cc. pyridine and benzoyl chloride (1 mol) was added under cooling. The mixture was then set aside overnight and the benzoylated substance was precipitated with water. The precipitate was then collected and recrystallized from the mixture of alcohol and acetone. M. p. 194.5° The yield was ca. 70%. The analysis coincides well with the calculation for monobenzoyl-compound. (Found: C, 61.15; H, 4.89%. Calc. for $C_{28}H_{27}O_5NBr$: C, 60.94; H, 5.08%)

The ester was hydrolysed to the original substance (m. p. 171°), when boiled with sodium carbonate in pyridine.

B. Reduction of 1-bromo-sinomeneine with PtO_2+H_2 in pyridine solution One gram of 1-bromo-sinomeneine was dissolved in 20 cc. of pyridine and 0.05g. PtO_2 was added. In shaking the flask in the hydrogen atomosphere at 1 atm. and 26-27°, ca. 100 cc. hydrogen was absorbed in three hours and the reaction came almost to a standstill. As the pyridine alone had absorbed ca. 40 cc. hydrogen in a blank test, the net volume of hydrogen absorbed amounted to 56.5 cc. (at N. T. P.), corresponding to one molecular equivalent (calc. 55 cc.). The platinum black was then filtered off and the solution was concentrated in vacuum. The residue was dissolved in 5% acetic acid and filtered quickly. The filtrate was made alkaline with 11% caustic soda solution and was shaken four times with ether. The treatment of the ethereal residue was done as described under (A), and 1-bromo-sinomeneine alcohol (m. p. 171°) was obtained in 10-20% yield The m. p. was unaltered by admixture with the specimen prepared by the aluminium isopropylate method.

When the above mentioned caustic soda solution was saturated with carbon dioxide and extracted with chloroform, a substance which melts at 216° was obtained. The melting point was, however, raised to 235°, when recrystallized from chloroform and alcohol. The yield was 10-20%.

It gave a green color with ferric chloride and formed a semicarbazone of m. p 250-256° and methiodide of m. p. 224° (dec.). These facts indicate that we have here 1-bromo-dihydrosinomenine.[5]

(2) Rearrangement of 1-bromo-sinomeneine alcohol into 1-bromo-sinomeninone

This was effected under various concentration of hydrochloric acid with varying yields. The best yield was described in the theoretical part. Dilute acetic acid seems to effect this change very slowly, or not at all. (compare (4)).

(3) Acetolysis of 1-Bromo-sinomineine alcohol

0.7g. of the substance was boiled with 0.7g. of sodium acetate and 7cc. of acetic anhydride for eight hours. After the solution was concentrated to a syrup in vacuum, a quantity of water was added, the precipitate was collected (ca. 0.7g.) and recrystallized from glacial acetic acid. M. p. 186° (also, the mixed melting point with 1-bromo-diacetyl-sinomenol of different origin).

Analysis. Found: C, 55.71; H, 3.921; CH_3O, 13.90%. Calc. for $C_{20}H_{17}O_6Br$: C, 55.43; H, 3.92; CH_3O, 14.31%.

(4) Catalytic reduction of 1-bromo-sinomeneine-alcohol

By the catalytic reduction of 1-bromo-sinomeneine alcohol with Pd-SO_4Ba as catalyst in a weakly acidic (hydrochloric or acetic) solution, we obtained (a) sinomeninone, when only one mol of hydrogen was absorbed, and (b) α- and β-dihydrosinomeninones, when two mols of hydrogen was utilized. Sinomeninone was identified with its melting point (151°, when dried over P_2O_5 in vacuo at 100°), with melting point of the iodomethylate (M. p. 265°), with elemental analysis, with methoxyl determination (two, one from crystal methanol) as well as with its decomposition into 3-methoxyl-4, 6-acetoxyl-phenanthrene. It is clear that the weak acidity of the solution first converted the substance into bromo-sinomeninone and the debromination followed.

α- and β-Dihydrosinomeninone are only the further reduction product of the sinomeninone. The remarkable fact here is that the 2% acetic acid effected the conversion of the substance into the 1-bromo-sinomeninone in this case. Seeing that the time elapsed in this reduction amounted to more than 24 hours and that the debromination necessarily gave rise to some hydrobromic acid, the above change does not seem to be exceptional.

(5) Reduction of some other sinomenine derivatives with aluminium isopropylate

The experimental condition was the same as was given in ((1) A). The results are summarized as follows:

(i) Sinomenine (4g.) Starting material was recovered more than 50%. No other crystalline substance was isolated from mother liquor.

(ii) 1-Bromosinomenine hydrochloride (6g.) Starting substance was recovered in 10%, besides a small amount of a substance of m. p. 216°, which was not further examined.

(iii) (+)-1-Bromo-dihydro-codeinone (4.4g.) Four grams of non-phenolic base (m. p. 188°) was obtained, but not investigated further.

(iv) 1-Bromo-sinomeninone Reduction took seven hours. Ether took up almost nothing from the caustic alkali solution. Chloroform extraction from soda alkaline solution, gave 2.3g. of mixed bases. Acetylation of this mixture gave a minute quantity of a substance of m. p. 184°. This melting point coincides with that of triacetate of 1-bromo-tetrahydro-sinomeninone prepared for comparision.[6] The mixed melting point was also unaltered. This proves that in 1-bromo-sinomeninone, its both ketonic groups were reduced by aluminium isopropylate in a small degree.

(5) This Bulletin, **4**, 197 (1929)

(6) K. Goto and T. Arai, This Bulletin, **17**, 116 (1942)

(6) Catalytic reduction of sinomenine and 1-bromo-sinomenine with PtO_2+H_2 in pyridine solution

Conducted as given in ((1) B).

(i) Sinomenine (1g.) was reduced with PtO_2 (0.2g.) in 20cc. pyridine. Temperature 25-26°. It took 2-5 hours to absorb 120cc. hydrogen (calc. 136cc. for $2H_2$). Yield: dihydro-sinomeninol (F. 160-162°) in 60%.(7)

(ii) When only 0.05g. PtO_2 was used in the same experiment, one mol of hydrogen was absorbed in three hours. Yield: dihydro-sinomenine (m. p. 198°) in 50-60%. Also, it was identified as oxime (m. p. 212-213°).

(iii) 1-Bromo-sinomenine (1g.) was reduced in the same condition as in (ii). One mol of hydrogen was absorbed in three hours. Yield: 1-bromo-dihydro-sinomenine (m. p. 235°) in 20-30%. Its semicarbazone showed the correct melting point 248-250°.

The reduction seems thus largely to depend upon the quantity of the catalyst used. When the catalyst was used in a small quantity, the reduction stopped after the hydrogenation of the double linkage, while in larger quantity the ketonic group is reduced to alcoholic also. This is a direct contradiction to the reduction of 1-bromo-sinomeneine, in which the ketonic group is reduced in prior to the double linkage. This may be due to the influence of the oxide-ring. We have already met with the similar phenomenon in the aluminium isopropylate reduction (compare (5)).

(7) Oxidation of 1-bromo-sinomeneine alcohol to 1-bromo-sinomeneine

A. With CrO_3. 0.1g. CrO_3 was dissolved in 10 cc. of acetone. One third of this solution was dropped slowly into 10cc. of acetone solution containing 0.2g. of 1-bromo-sinomeneine alcohol, at room temperature. The brown precipitate was filtered off and the filtrate was concentrated until crystals separated. The crystals (m. p. 180-200°) were dissolved in chloroform and the solution was washed with dilute caustic soda. To the concentrated chloroform solution, a large quantity of alcohol was added to make 1-bromo-sinomeneine crystallize out. M. p. 214°, also admixture with 1-bromo-sinomeneine prepared by bromination method. Yield 40%. Analysis. Found: C, 55.86; H, 5.13; N, 3.20%. Calc. for $C_{19}H_{20}O_4NBr$: C, 56.11; H, 4.93; N, 3.45%.

B. With $KMnO_4$. 1-Bromo-sinomeneine alcohol (0.2g.) was dissolved in acetone (10cc.) and $KMnO_4$ (0.08g.) was added little by little during 1.5 hours. MnO_2 was filtered off, and the solution was concentrated. Dilute caustic soda was added and 1-bromo-sinomeneine was extracted three times with chloroform. The purification was carried out as above, but the melting point was somewhat lower (210°). The base was therefore turned into its methiodide, which showed the correct melting point 211° (also the mixed melting point). Yield of the base 20%.

The 1-bromo-sinomeneine alcohol was not, however, acted by H_2O_2 in acetic acid or by NaOBr in a mild condition.

Our thanks are due to Miss Yoshiko Suzuki of our laboratory (Agricultural Department), who helped us in carrying out some of the micro-analyses in this work.

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Agricultural Department, the University of Tokyo and the Kitasato Institute.

Absorption of Nitrogen by Zirconium and Iron

By Shizuo FUJIWARA

(Received August 19, 1949)

Zirconium is one of the elements which are said to have good effect of denitrogen, deoxygen, etc., when added in steel. It is used, also, as a getter in the vacuum-tube. These are owing to its great affinity to metalloid atoms.

It is the object of the present papers to investigate in detail the characateristics of the nitrides formation of zirconium, ferro-zirconium and pure iron, which will make a contribution to the problems concerned to the use of this element.

Experimental

The increase of the weight of the samples (zirconium-metal, ferro-zirconium and pure iron) which was resulted from the progress of the nitrogen absorption with the samples, was measured.

The dish containing the sample was hanged vertically with a spring balance and the whole was settled in a tube. All of the equipments, the dish, the spring balance and the tube, were made of fused silica. The stream of the purified nitrogen was sent into the tube which was heated in an electric furnace.

As the sample absorbed nitrogen at some temperature, the balance stretched and the stretched length was measured with the telescope of the cathetometre, and then temperature was gradually raised. Increase of 1 mg. in weight corresponded to 0.628 ± 0.002 mm. of

(7) K. Goto and S. Mitsui, This Bulletin, **5**, 282 (1930)

the stretched length, Δl.

Results

Samples . Zr-metal : amorphous, black powder made in Japan.
Fe-Zr: „ „
Iron : powder of reduced iron made by Kahlbaum Co.

In Table 1 the compositions of the samples are given.

Table 1

Sample		Zr cont. (total %)	Zr % (as carbides)	Zr % (as oxides)
Zr-metal	No. 114	94.0	4.9	6.0
	103	84.0	49.3	—
	131	96.7	7.3	21.2
	133	96.5	3.9	29.9
Fe-Zr	40	28.1	2.8	0.4
	44	29.9	4.0	3.1

Experiments Expt. No. 1—Zr-metal No. 114. Sample taken : 100.5 mg. The reaction between Zr and nitrogen began in the range of 265°-290°C and then continued linearly as the temperature was raised and the time passed. The temperature was raised up to 1000°C during 6 hours. (Table 2).

Table 2

Expt. No. 1			Expt. No. 2		
T°C	t min.	Δl mm. (×1/100)	T°C	t min.	Δl mm. (×1/100)
265	85	0	470	120	0
290	96	25	520	130	20
400	199	235	620	186	85
450	240	350	〃	220	205
520	250	390	〃	260	465
650	298	515	700	265	490
760	323	589	760	275	565
870	330	679	850	281	620
920	365	870	940	290	640
1020	368	919	950	310	740

Expt. No. 3			Expt. No. 4		
T°C	t min.	Δl mm. (×1/100)	T°C	t min.	Δl mm. (×1/100)
100	10	0	250	67	0
400	35	75	280	77	35
〃	100	100	300	164	175
〃	295	340	〃	307	315
〃	518	765	〃	407	425
600	559	780	500	542	555
770	576	740	800	557	585
7.0	616	〃	850	602	620
880	626	720	900	610	605
900	636	690	〃	620	595
940	645	725	〃	627	585
910	655	750	1030	632	595
900	677	780	〃	662	625
〃	685	710	〃		
〃	725	〃			
950	733	750			
1010	744	750			

T°C .....temperature where the experiment was carried out
t min. ...the time since the start of the experiment
Δl mm....stretching of the spring balance

Expt. No. 2—Zr-metal No. 103. Sample taken : 109.0 mg. It is strange that the beginning-temperature of the reaction lies between 470°C and 520°C and differs from those of the other samples (No. 114, 131, 133) which react at 265° -290°C.

This would be due to the special condition of the sample, because, while all the other samples were produced through reduction with carbon or sodium metal, the present one was made by alumino-thermit method and would have been affected by aluminium in some way.(1)

Expt. No. 3—Zr-metal No. 131. Sample taken : 111.5 mg. In this case, the decomposition occured at 600°C and the decrease of the weight of the sample was observed. This decreasing tendency continued up to 900°C. Just above 900°C, the length of the spring balance once increased and then the decreasing tendency began again (Table 2).

Similar decreasing tendency at 900°C was also observed in the case of the sample, Zr-metal No. 133, in Expt. No. 4.

The present author has found by chemical analysis that the decomposition or the transformation of carbides into nitrides occur at 700°C and 900°C in the researches concerning the metalloid compounds of zirconium and hafnium.(2) The results found here seem to correspond to that phenomenon.

Expt. No. 4—Zr-metal No. 133. Sample taken : 76.6 mg.

Expt. No. 5—Fe-Zr No. 44. Sample taken : 115.2 mg.

Expt. No. 6—Fe-Zr No. 40. Sample taken : 131.1 mg.

The most distinctive character of the Fe-Zr that makes it different from Zr-metal is the temperature where the absorption of nitro-

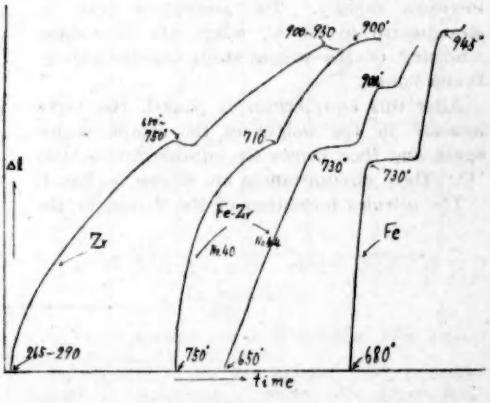

Fig. 1

(1) Aluminium begins to absorb nitrogen at 600° ~700°C. (K. Iwase, *Sci. paper. Tohoku Univ.*, **15**, 531 (1926))
(2) S. Fujiwara, *J. Chem. Soc. Japan*, in press.

gen begins; it is 650°~750°C which is far higher than 265°~290°C, at which Zr-metal bagins to absorb nitrogen.

Moreover, in this case the absorption curve shows the breaks at 700°C and 900°C as shown in Fig. 1.

It must be emphasized that these temperatures where the absorption begins and the breaks occur exactly coincide to those for the pure metal of iron except that the curvature for Fe-Zr is greater and the figure of the absoption curve for iron is rather steep.

Expt. No. 7—Pure Iron. Sample taken: 163.0 mg. In the earlier stages of heating, the weight of the sample decreases as seen in Table 3. It would be due to the desorption of the moisture contained in the sample.

Table 3

Expt. No. 5			Expt. No. 6			Expt. No. 7		
T °C	t min.	Δl mm. (×1/100)	T °C	t min.	Δl mm. (×1/100)	T °C	t min.	Δl mm. (×1/100)
630	165	0	700	114	0	200	16	−185
550	172	15	〃	131	130	〃	44	−215
700	191	65	〃	170	215	250	50	−255
〃	220	165	710	191	230	300	55	〃
740	245	185	〃	222	250	〃	76	〃
730	258	245	910	235	275	670	139	0
〃	290	〃	〃	250	295	680	144	20
820	308	〃	〃	275	325	730	169	347
960	330	310	920	302	370	〃	179	372
970	345	〃	920	310	〃	〃	184	〃
〃	353	〃	〃	320	〃	〃	219	〃
〃	368	345				800	226	372
〃	380	360				940	244	457
						945	254	492
						〃	259	517
						〃	274	〃
						〃	284	〃
						〃	294	542

The absorption of nitrogen begins at about 650°C and then the weight of the sample increases rapidly. The absorption goes on straight up to 730°C, where the increasing tendency of the weight stops and the equilibrium comes.

After this equilibrium is passed, the rapid increase in the weight of the sample begins again and then comes the equilibrium at 945 °C. These circumstances are shown in Fig. 1.

The nitrides formation of the γ-iron in the range of 620° and 700°C has been found only by K. Iwase[1] among many workers. The results of the present author that the absorption begins at 650°C and the equilibrium is obtained at 730°C seem to coincide to those of K. Iwase.

Conclusion

The characteristic temperatures are summarized in Table 4 and in Fig. 1. Fe-Zr and

Table 4

	Zr-metal	Fe-Zr	Iron
Temp. where N_2 absorption begins	265 ~290	650 ~750	650
Temp. where 1st equilibrium begins	600 ~700	730	730
Temp. where 2nd equilibrium begins	900 ~950	900 ~960	945

iron coincide exactly both in the beginning temperature and the equilibrium temperature. These features may be attributed to the nitrogen absorption by α- and the γ-iron. The effect of zirconium in Fe-Zr may be seen in the gentle slope of the absorption curve for Fe-Zr No. 40, but it is not so distinct.

As zirconium has great affinity to the metalloid atoms, it begins to absorb nitrogen at as early as 260°C. Two breaks are observed in the absorption curve of Expt. No. 3 (Sample 131) and one in Expt. No. 4 (Sample 133). These breaks would represent some equilibrium, but the reactions occurring here would be different from those for pure iron and Fe-Zr, and as it could be found in the former case, the decrease of the weight was due to the decomposition of the samples.

The absorption curve goes on linearly with the rise of temprature in the case of Zr metal and is far less steep than those for iron and Fe-Zr. It may be concluded from all these results that the nitrogen absorption of the former is different from the latter.

The author wishes to express his hearty thanks to Prof. K. Kimura for his kind guidance and encouragement.

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On the Anomalous Melting Point and the Decomposition of Acetyl-salicylic Acid

By Yojiro TSUZUKI and Masako SAWADA

(Received September 2, 1949)

In Beilstein's Handbook Vol. X (1927) it is described that Bayer's aspirin is different in some respects from most preparations of acetyl-salicylic acid, namely, it has a crystalline form of plates, and shows a high melting point of 137°, while others are needles and usually melt at 135°. Some pharmaceutists,[1] having made comparative studies on a number of samples of acetyl-salicylic acid produced in France, Germany and in our country, came to the conclusion that our domestic products are not inferior to the imported ones. It was also shown[2] that the crystals of various domestic products consist of plates like those of Bayer's aspirin, although some difference is observed in crystalline habit according to makers, but, unfortunately, there lacks any description on their melting points.

Melting point Some papers have already been published[3] on the examination how the melting point of acetyl-salicylic acid varies with the solvents used for recrystallization, but the melting points described by them were always below 134°. With a view to reinvestigate this question, we have made recrystallization from various solvents and measured the melting points of the products.

The recrystallization was carried out by evaporating the solvents slowly at lower temperatures. The crystals separated out were usually plates like Bayer's aspirin, but sometimes there appeared prismatic crystals. The melting point was determined by putting a capillary tube with the sample suddenly in a bath heated up to 130° and by elevating the temperature of the bath at a rate of 4° per minute. The results are presented in Table 1, which shows that the melting point, being in most cases nearly 135°, reaches as high as 137°, when acetyl-salicylic acid is recrystallized from a hydrophobic solvent such as chloroform. Thus it may safely be concluded that Bayer's aspirin is not a special chemical substance in melting point nor in crystalline form.

Table 1

Solvent	m. p. (corr.)	Solvent	m. p. (corr.)
Chlofoform	136.3-137.4	Ethyl alcohol	135.1
Dioxan	135.7		
Acetic anhydride	135.7	Methyl alcohol	132.6-133.6
Ether	135.6	Water	131.6

(1) H. Suzuki, I. Keimatsu and K. Ito, *Chem. Abstr.*, **29**, 5429 (1935)

Decomposition It has already been recognized that acetyl-salicylic acid undergoes decomposition before it reaches its melting point, but the extent of thermal decomposition has never been measured. Hence we have measured the quantity of salicylic acid set free by thermal decomposition[4] of acetyl-salicylic acid, employing a newly devised colorimetric method of determining salicylic acid, since none of the known methods[5] is found quite suitable fo rour purpose.

The standard solution of our new method is made by adding 0.5 cc. of a 12 per cent aqueous solution of ferric chloride hexahydrate to 20 cc. of a 0.06 per cent methanol solution of salicylic acid containing 1 g. of acetyl-salicylic acid, whereby a brown color with a violet tint is developed, and compared by a 0.001 mol/l.

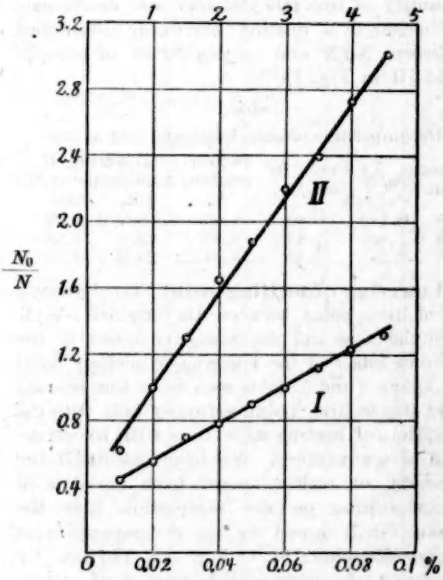

Fig. 1

(2) S. Watanabe and A. Watanabe, *Proc. Imp. Acad. Japan.*, **11**, 379 (1935)

(3) Capelli, *Pharm. Ztg.*, **65**, 800 (1920); K. Suda and H. Ogakureyama, *J. Pharm. Soc. Japan*, **No. 481**, 241 (1922) (in Japanese); Putnam, *Ind. Eng. Chem.*, **16**, 778 (1924)

(4) This expression is not quite right, the decomposition is rather hydrolysis due to moisture.

(5) Allport, "Colorimetric Analysis", p. 162 London (1947)

Duboscq colorimeter with a series of solutions of various concentrations prepared in a similar way. It has thus been found that a linear relationship exists between the concentration of salicylic acid and the ratio of the lengths of the two solutions, N_0/N, N_0 being that of the standard (I in Fig. 1). In Table 2 are shown the results of experiments made at 110° with 1 g. of acetyl-salicylic acid.

Table 2

Decomposition of acetyl-salicylic acid.

Time min.	N_0/N	Conc. %	Decomposition %	Lowering of melting point obs.	calc.
5	0.613	0.025	0.65	1	0.48
15	0.672	0.031	0.79	4	0.57
25	0.925	0.053	1.38	4	1.02
35	1.093	0.068	1.77	5	1.30

In Table 3 are shown the results of measurements made at 128°. In this case 0.2 g. of acetyl-salicylic acid was used. After heating at this temperature for a definite length of time it was dissolved in 20 cc. methanol and 0.5 cc. of a 1/2 mol aqueous solution of ferric chloride was added to it. By comparing this solution colorimetrically with the standard made from a 1/1000 mol methanol solution of salicylic acid and the iron reagent, the quantity of free salicylic acid was determined by means of a relation previously established between N_0/N and concentration of salicylic acid (II in Fig. 1).[6]

Table 3

Decomposition of acetyl-salicylic acid at 128°

Time min.	N_0/N	Conc. 10^2 mol/l.	Decomposition %	Lowering of melting point (°C) obs.	calc.
5	0.719	0.60	1.08	2	0.79
15	1.825	2.45	4.41	13.5	3.23
25	2.23	3.25	5.81	20.5	4.22

Lowering of melting point The difference in melting point between the original acetyl-salicylic acid and the heated is shown in the column (obs.) of the lowering of melting point in Tables 2 and 3. It is seen from this column that the melting point naturally falls with the duration of heating as well as with the elevation of temperature. We have calculated the lowering of melting point from the data of decomposition on the assumption that the depression is caused by the decomposition of acetyl-salicylic acid. For this pnrpose we measured the molecular depression of acetyl-salicylic acid by using adipic acid, salicylic acid and hydroquinone as solutes. The results of measurements are shown in Table 4.

The calculated values of lowering of melting point shown in Tables 2 and 3 were obtained from the data of decomposition by using 6.6 as the mean value of molecular depression. The observed values, as may be seen, are always incomparably larger than the calculated. Hence it seems to us that the abnormal depression of melting point of acetyl-salicylic acid is not solely due to the dissolution of both salicylic and acetic acids formed by its thermal decomposition.

Table 4

Molecular depression of acetyl-salicylic acid.

Solute	Conc. %	Depression	Molecular depression
Adipic acid	15	6.66	6.48
〃	30	13.33	6.49
Salicylic acid	13.8	6.50	6.50
〃	27.6	12.75	6.38
Hydroquinone	11	6.75	6.75
〃	22	14.00	7.00
			Mean 6.6

Anomalous melting point Such an anomalous behavior in melting point is observed not only in acetyl-salicylic acid, but also in its *p*-isomer, namely, *p*-acetoxy-benzoic acid. As the melting point of this compound is variously recorded in the literature, we have examined it with some materials obtained by recrystallizing from various solvents such as ether, acetic anhydride, ethyl alcohol, methanol, dilute alcohol, and water, and have found it to lie between 186° and 188°. The discrepancy, though much smaller than in acetyl-salicylic acid, is yet clearly seen. A sample of *p*-acetoxy-benzoic acid, once melted, shows a depression by 2° to 3°. By repeating this process fifteen times, we have realized that the melting point can be lowered finally even to 165°. This depression is undoubtedly associated with thermal decomposition of *p*-acetoxy-benzoic acid. While on the contrary, both free salicylic and free *p*-hydroxy-benzoic acids show no sign of this phenomenon. Their melting points are quite definite, exhibiting no tendency of lowering, even if repeatedly melted.

Thus it was confirmed that the lowering of melting point is exclusively due to the instability of their acetyl derivatives.

We have in the next place made comparison in stability between the *o*-and *p*-compounds, since it appers to us that acetyl-salicylic acid is more liable to decomposition than its *p*-isomer. According to the measurements of Anschütz and Motschmann[7] the velocity constants of hydrolysis of acetyl-salicylic acid in water at 100° is 0.14701 (t=30 min.), while that of the *p*-isomer is 0.05975. We have also found that the saponification velocity constants of *o*-and *p*-acetoxy-benzoates in boiling dilute alcohol are respectively 0.015 and 0.0015 (t= min.). Thus it is clear that *p*-acetate is far

(6) The line I is related with the lower ordinate, the line II with the upper. The concentration is exprssed in different measures, so as to fit the lines into a diagram.

(7) Ann., **392**, 116 (1912)

resistent to decomposition than acetyl-salicylic acid. Besides, in harmony with this fact, a wide difference is observed between the velocities of formation of the two acetyl derivatives, viz., it takes more than three hours to obtain the *p*-compound by boiling a mixture of hydroxy-benzoic acid and acetic anhydride, whereas it takes only one hour with acetyl-salicylic acid. Thus it is evident that acetyl-salicylic acid is more easily formed and more liable to be decomposed.

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Analytical Chemistry by Means of Organic Compounds XIV
Electrolytic Reduction of Organic Reagents at the Dropping Mercury Cathode and Its Application to Amperometric Titrations — 8-Hydroxyquinoline* (1)

By Masayoshi ISHIBASHI and Taitiro FUJINAGA

(Received September, 13, 1949)

Many organic compounds are reducible at the dropping mercury electrode, so the organic reagents which precipitate metal ions are very useful in the amperometric titrations. Kolthoff and his coworkers have been greatly instrumental in developing these titrations.(1) In the meantime, we also introduced this titration method and described some examples of our works(2) in which organic reagents were applied to it.

In the present paper, the behavior of electrolytic reduction of 8-hydroxyquinoline at the dropping mercury electrode is discussed and in the subsequent paper, the amperometric titration of magnesium, copper etc. with that reagent will be introduced.

Experimental

Chemicals and Apparatus Used Oxine (8-hydroxyquinoline) made by Takeda Chemicals Co. was twice steam-distilled and dissolved in pure dilute ethyl alcohol. Magnesium carbonate, ferric nitrate and zinc sulfate were Merk or Kahlbaum's "zur Analyse". The c. p. copper sulfate was twice recrystallized. They were all examined in their purity by the polarographic method. Buffer solutions from pH = 2.2 to 12.0 were Kolthoff, Vleeshhower's.(3) pH = 1.0 and pH = 13.0 were 0.1 N hydrochloric acid and sodium hydroxide respectively. The polarograph used is a Heyrovsky-Shikata type made by Yanagimoto Co., Kyoto.

Polarographic Behavior of Oxine Polarograms of oxine in various pH solutions are shown

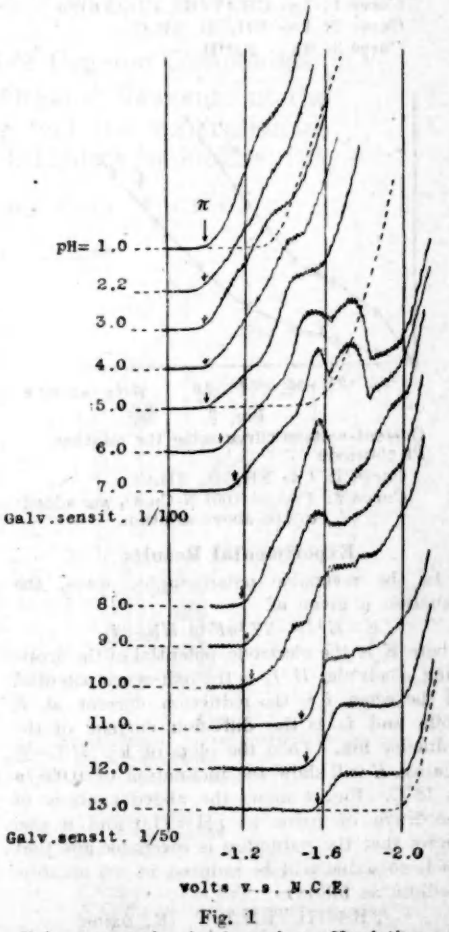

Fig. 1
Polarograms of oxine in various pH solutions

* Presented at the annual meeting of the Chemical Society of Japan in 1948 and the annual meeting of the Research Institute of Chemistry, Kyoto University in 1947.

(1) I. M. Kolthoff *et al*, *J. Amer. Chem. Soc.*, **61**, 3402 (1939). ibid, **62**, 211, 3332, etc, (1940)

(2) M. Ishibashi and T. Fujinaga, "Polarography in Inorganic Analysis" in "The Review of Analytical Chemistry (in Japanese)" Vol. 2 Kyoritsusha publ. Co., Tokyo (1944)

(3) I. M. Kolthoff, "Acid-base Indicators", Macmillan Co. (1937)

in Fig. 1. These solutions have the composition of 10^{-3} M-oxine, 10^{-3} M-KCl and some tylose, except buffer agents. For the amperometric purpose, the polarograms of oxine in 1 N-NH_4OH, NH_4Cl and 1 N-CH_3COOH, CH_3COONa are researched (Fig. 2). Current-voltage curve of copper sulfate in 1 N-NH_4OH, NH_4Cl by using the platinium rotating electrode are also shown in Fig. 3.

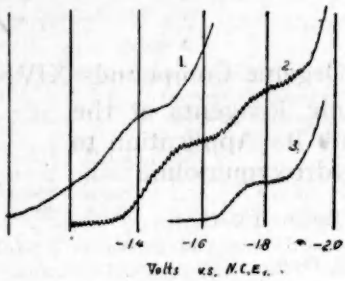

Fig. 2
Polarograms of oxine in some buffer solutions
Curve 1: 1 N- CH_3COOH, CH_3COONa
Curve 2: 1 N- NH_4OH, NH_4Cl
Curve 3: 0.1 N- NaOH

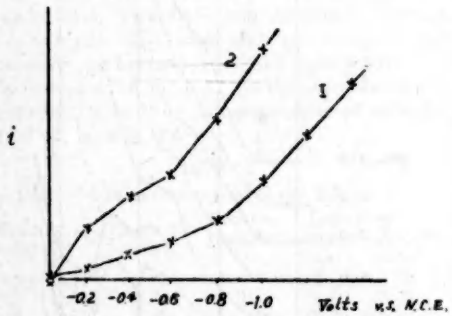

Fig. 3
Current-voltage curve using the rotating Pt electrode
Curve 1: 1 N- NH_4OH, NH_4Cl
Curve 2: 1 ml. of 0.001 N-$CuSO_4$ was added to the above solution.

Experimental Results

In the reversible polarographic wave, the equation is given as

$$E = E^{1}/_{2} - RT/nF \cdot \ln i/(i_d - i)$$

where E is the electrode potential of the dropping electrode, $E^{1}/_{2}$ is the half-wave potential of the wave, i is the reduction current at E volts and i_d is the diffusion current of the reducible ion. Then the plots of $\log i/(i_d - i)$ against E will show the inclination of $0.058/n$ at 18°C. Fig. 4 shows the above analysis of the wave of oxine at pH=11.0 and it also shows that the reduction is reversible and that $n \doteqdot 1$, so oxine will be reduced in the alkaline medium as follows.

$$2R + 2H = RH_2R \qquad (R: \text{oxine})$$

which is analogous to meriquinone formation.

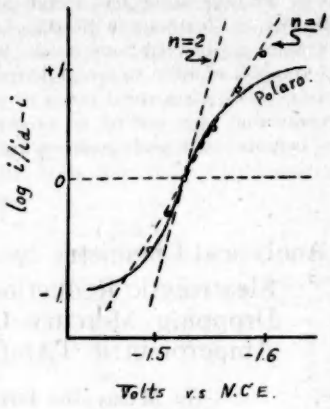

Fig. 4
Analysis of the polarographic wave of oxine at pH=11.0

With decreasing pH, the reduction becomes complicated and irreversible, so each polarogram becomes to produce characteristic maximum respectively whose behavior is analogous to quinoline[4] and so the reduction current of oxine is chiefly due to the quinoline nucleus. The addition of tylose suppresses the maximum but could not eliminate it even in its higher concentration.

In the acidic medium the reduction is also irreversible and the plots of $\log i/i_d - i$ against E does not give straight line and in these medium the deposition of hydrogen seems to be catalytically urged, comparing with the blank wave (the dotted curves in Fig. 1).

The relation of pH to the reduction potential of oxine π are shown in Fig. 5, where π is not the half-wave potential, but the potential at which 45° tangent touches the curve. Assuming

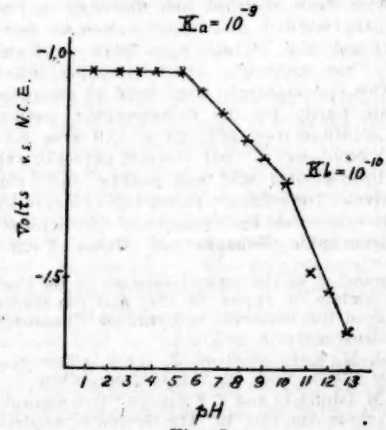

Fig. 5
Relation of the reduction potential π to pH

(4) I. Tachi and H. Kabai, *J. Electrochem. Association Japan*, **3**, 1 (1935)

the π to be the parallel value to the standard reduction potential, the bending points will be the position of $pH = pK_a$ and $pH = pK_b$ respectively and it becomes $K_a = 10^{-9}$ and $K_b = 10^{-10}$. These dissociation constants coincide with Kolthoff's data.[5]

In ammoniacal solution, the diffusion current of the first wave of oxine is reached at $E_c = -1.60$ volts v. s. normal calomel electrode and at this potential the diffusion current of oxine is proportional to its concentration. In 0.1 N-NaOH, the same condition is found at $E_c = -1.80$ volts v.s. N.C.E. In acetic acid acetate medium, the short diffusion current range is found at $E_c = -1.40$ volts and the diffusion current of oxine is proportional to its concentration only in the limited concentration range.

These medium were used in the amperometric titration of magnesium, copper, etc. with oxine and it will be discussed in the subsequent paper.

Using the platinium rotating micro-electrode,[6] the oxine was not reduced before the hydrogen deposition even in the ammoniacal solution, but the copper was reduced (see Fig. 3).

Summary

The behavior of electrolytic reduction of oxine at the dropping mercury electrode was discussed. The reduction of oxine in alkaline medium is simple and reversible at the electrode and the possibilities of amperometric titrations with oxine in these mediums were researched.

Institute of Chemistry, Faculty of Science, Kyoto University.

(5) I. M. Kolthoff, *Chem. Weekbl.*, **24**, 606 (1927)
(6) I. M. Kolthoff and W. E. Harris, *Ind. Eng. Chem. Anl. Ed.*, **18**, 161 (1946)

Analytical Chemistry by Means of Organic Compounds XV Electrolytic Reduction of Organic Reagents at the Dropping Mercury Cathode and its Application to Amperometric Titrations—8-Hydroxyquinoline (2)

By Masayoshi ISHIBASHI and Taitiro FUJINAGA

(Received September 13, 1949)

In the previous paper, the behavior of electrolytic reduction of oxine were investigated and it was seen that the waves of oxine were well-defined in ammoniacal and alkaline medium and ill-defined in acidic medium. These were applicable to the amperometric titration of magnesium, copper, zinc and iron.

Experimental

Titration was carried out with the apparatus shown in Fig. 1. The manipulation of the titration was as follows. A measured volume (usually 20 ml.) of the standard sample solution in the proper medium was introduced into the cell and hydrogen gas was passed through for thirty minutes. The proper e. m. f. was applied to the cell and the current was measured. Alcoholic oxine solution was added successively with a microburette. After each addition the content of the cell was mixed by passing hydrogen gas for half a minute and the current was recorded after it became constant (after one or two minutes). In all cases the values of the current, corrected for the volume change, were plotted against the amount of reagent added. A small ordinary beaker was used as a titration cell, which was not closed when the concentration of metals was larger than about 10^{-3} M. However it was necessary to keep on stirring by hydrogen gas, except the case of measurement.

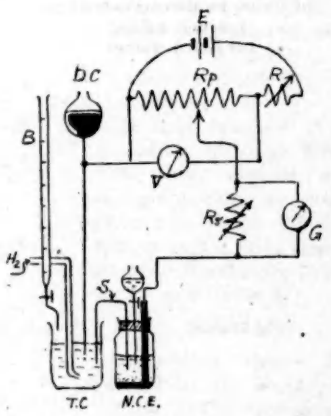

Fig. 1
Apparatus of amperometric titration
E: accumulator
R_p: potentiometer
R: variohm
V: voltmeter
G: galvanometer
R_s: shunt of galvanometer
D.C.: dropping mercury electrode
T.C.: titration cell
N.C.E.: normal calomel electrode
B: burette
S: salt bridge

Titration of Magnesium From the preliminary experiments, it was decided to carry out the titration of magnesium in a medium of ammonium chloride and ammonia. With the normal calomel electrode as anode, the applied e. m. f. was −1.60 V., so the first wave of oxine was used in the titration. In this medium the proportionality of diffusion current of oxine to its concentration was satisfactory (see Fig. 2). Results obtained in the titration of magnesium solutions are given in Table 1. Reverse titration was also agreeable. Calcium, when its amount was very small did not interfere with the titration. When its amount was large, high results were found. However, if ammonium oxalate was added in excess, the correct result was obtained, when separation of calcium oxalate was not necessary before the titration.

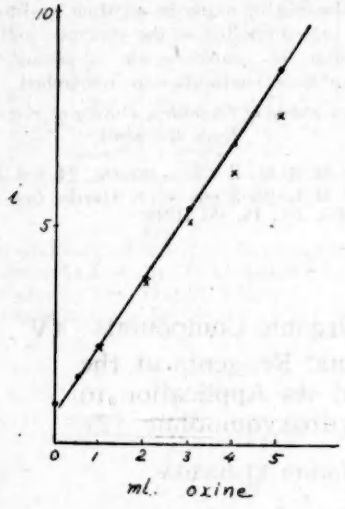

Fig. 2
The proportionality of diffusion current of oxine to its concentration
× observed values
• corrected values

Application of this titration to the analysis of magnesium in aluminium alloy, brine and sea-water were successful (Table 2). Aluminium alloy was dissolved in sodium hydroxide and the residue was dissolved in hydrochloric acid and ammonium hydroxide solution was added in excess. Then hydrogen sulfide was bubbled to precipitate other heavy elements and titrated with oxine without separating the precipitate. These sulfides did not interfere with the titration at this applied potential. Brine contains little calcium. Sea water contains calcium about 0.4 g. per litre, while calcium oxinate is slightly soluble when ammonium salts is present,[1] and by the salt effect of supporting electrolyte and sea-water, the direct titration was possible without adding ammonium oxalate.

Table 1
Titration of magnesium with oxine

No.	Mg used	Ca added	Oxine used	Factor of oxine	Mg found	Error
	mg.	mg.	ml.		mg.	%
1	4.30	0	6.38	0.672	4.287	−0.3
2	6.45	0	9.75	0.672	6.431	−0.3
3	8.60	0	12.77	0.672	8.581	−0.2
4	6.08	0	9.00	0.672	6.048	−0.5
5	4.30	20	6.35	0.672	4.267	−0.7
6	4.30	40	6.35	0.672	4.267	−0.7

* No. 1, 2 and 3 are mean value of several titrations.
* No. 4 is reverse titration (oxine was titrated with magnesium).
* In No. 5 and 6, ammonium oxalate was added in excess before titration.

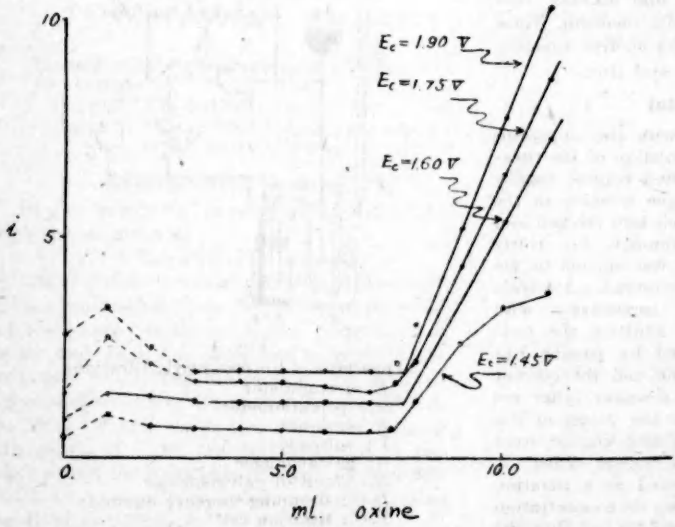

Fig. 3
Titration of magnesium in sea-water with oxine at various applied potentials

These samples were gravimetrically analysed as magnesium pyrophosphate. In this case calcium in sea water was eliminated as calcium oxalate. Sea water used was collected near Suma in the bay of Osaka and its chlorinity was 15.74. The magnesium content obtained in this experiment showed very good coincidence with that calculated from the Wattenberg's

(1) R. Berg, *Z. anal. Chem.*, **71**, 23 (1927)

data[2] (Table 3).

Table 2

Titration of magnesium in various samples

Sample No.	Oxine taken ml.	Factor of oxine	Mg found (Ampero.) mg.	Mg found (Gravi.) mg.	Error %
1. Al-alloy					
998.1mg.	7.30	0.680	4.964	4.742	+4.0
1006.1mg	7.05	0.680	4.794	4.778	+0.3
2. Brine					
0.20 ml.	28.30	0.672	19.02	19.05	−0.2
0.10 ml.	14.10	0.672	9.48	9.53	−0.5
3. Sea water					
5.00 ml.	8.05	0.680	5.474	5.456	+0.3
5.00 ml.	8.00	0.680	5.440	5.456	−0.3
5.00 ml.*	8.00	0.680	5.440	5.456	−0.3

* Calcium was precipitated as calcium oxalate.

Table 3

Magnesium content in sea-water

Mg in kg. of sea-water (by Wattenberg) Cl = 19.00 % g.	Mg in ml. of sea-water (calc. from Wattenberg) Cl = 15.74 % mg.	Mg in ml. of sea-water (Ampero. titr.) Cl = 15.74 % mg.	Error %
1.280	1.086	1.0882	0.2

Titrations of Iron, Zinc and Copper and Their Differential Titrations Ferric oxinate is quantitatively precipitated from the tartrate solution,[1] but this was not applicable for the titration, because the precipitation is complete only when the excess reagent is added. However we found that ferric iron dissolved in excess of ammonium carbonate reacts stoichiometrically with oxine and this medium is applicable for the titration. Copper was titrated in a medium of ammonium chloride—ammonia at $E_c = -1.60$ V. and sodium acetate-acetic acid at $E_c = -1.40$ V. and also titrated in ammoniacal medium using the rotating platinium wire electrode at $E_c = -0.40$ V. See Fig. 4. Zinc was titrated in the same medium as copper and in 0.1 N-sodium hydroxide at $E_c = -1.80$ V. The reduction of oxine in acidic medium is irreversible and the diffusion current of oxine is only proportional to its concentration in the small concentration range. Therefore, after passing the end point, it is difficult to get a straight line any more.

Next, it was attempted to titrate iron, zinc and copper, differentially when they are present altogether. Sample should be divided into three parts. To the first part we added ammonium carbonate in excess until precipitate of basic carbonate redissolved and titrated at $E_c = -1.60$ V (A cc.). To the second part ammonium chloride and ammonia were added to precipitate ferric hydroxide and the solution was titrated at $E_c = -1.60$ V (B cc.). To the last part, after heating to boiling, sodium hydroxide was added to precipitate copper and iron and the titration was carried out at $E_c = -1.80$ V after cooling the solution (C cc.).

Then the concentration of each component will be calculated from the next equations:

$$[Fe] = X(A-B)$$
$$[Cu] = X(B-C)$$
$$[Zn] = XC$$

In these equations X is the normality of oxine solution. This work, however, is only the preliminary one and the error was about 5% in the determination of zinc and copper. Results are shown in Fig. 5 and Table 4.

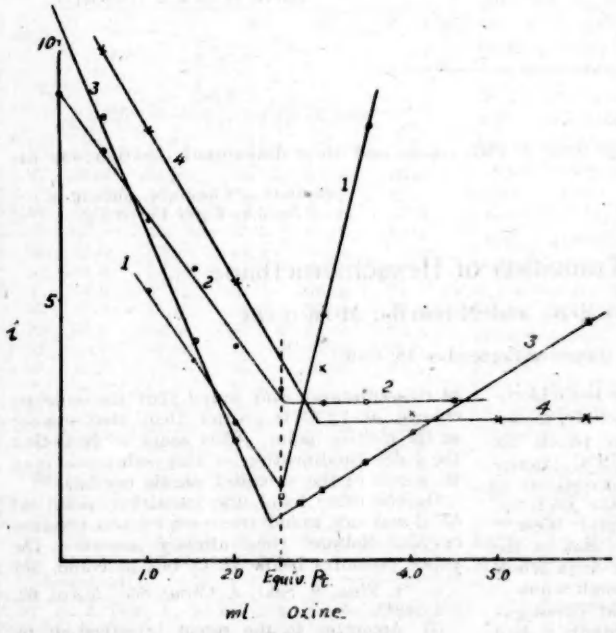

Fig. 4

Titration of copper with oxine

Curve 1 : No. 2 in Table 4 Curve 2 : No. 5 in Table 4
Curve 3 : No. 3 in Table 4 Curve 4 : No. 4 in Table 4
(Pt electrode at $E_c = -0.4$ V)

Summary

Magnesium was directy titrated by the amperometric method. The accuracy was 0.7% or better with 10^{-3} M concentration of magnesium. Its application to the analysis of alloy, brine and sea-water were studied. The interference of calcium and its elimination are described.

(2) H. Wattenberg, *Z. anorg. allgem. Chem.*, **236**, 46 (1938)

Table 4

Titration of coppr, zinc and iron

No.	Metal taken mg.	Medium	Oxine used mg.	Conc. of oxine N	Metal found mg.	Error %
1.	3.369 Cu	Amm. chl.	5.00	0.0211	3.353	− 0.4
2.	1.685 Cu	Amm. chl.	2.48	0.0211	1.663	− 0.3
3.	0.1685 Cu	Amm. chl.	2.42	0.00211	0.1622	− 3.2
4.	0.0337 Cu	Amm. chl.	2.90	0.000422	0.0388	+15.04
5.	1.685 Cu	Amm. chl.	2.48	0.0211	1.663	− 1.3
6.	1.685 Cu	Acet. ac.	2.50	0.0211	1.676	− 0.5
7.	1.798 Zn	Amm. chl.	2.60	0.0211	1.793	− 0.3
8.	1.798 Zn	Acet. ac.	2.59	0.0211	1.791	− 0.4
9.	1.798 Zn	Sod. hyd.	2.60	0.0211	1.793	− 0.3
10.	1.033 Fe	Amm. carb.	2.64	0.0211	1.042	+ 0.9
11.	1.685 Cu 1.798 Zn	Amm. chl.	5.12	0.0211	.....	+ 0.0
12.	1.685 Cu 1.798 Zn	Sod. hyd.	2.44	0.0211	1.683 (Zn)	− 4.7
13.	1.033 Fe 1.685 Cu 1.798 Zn	Amm. carb.	7.75	0.0211	.....	+ 0.01

* In No. 5, the rotating platinium electrode was used.
* In No. 12, copper was precipitated as cupric oxide.

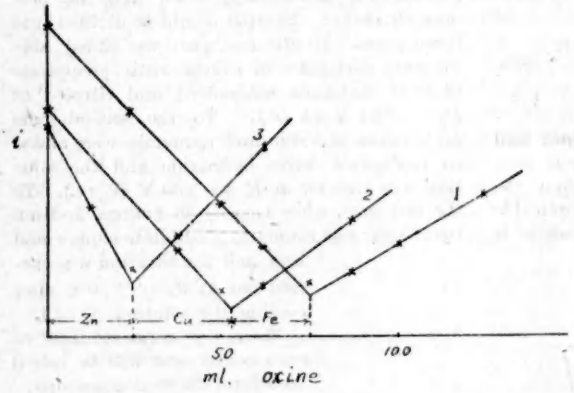

Fig. 5

Titration of mixture of iron, zinc and copper with oxine

Curve 1: in 2 N-$(NH_4)_2CO_3$
Curve 2: in 1 N-NH_4OH, NH_4Cl
Curve 3: in 0.1 N-NaOH

Iron, zinc and copper were also titrated with oxine and their differential titration was investigated.

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Heats of Transition of Hexachloroethane

By Syûzô Seki and Masanobu Momotani

(Received September 13, 1949)

It is known that the crystalline hexachloroethane has three modifications; triclinic, monoclinic and cubic. The transition points are 45°C (triclinic∼monoclinic) and 72°C (monoclinic∼cubic), respectively. X-ray investigations of these transition phenomena have been already undertaken by Finback[1] and West,[2] of whom the former concluded that in the cubic modification the molecules as a whole are in the rotational motion in a rough sense.

In connection with the structual investigations, Nitta and one of the authors[3] had several years ago measured the vapor pressures of this substance and found that the entropy change at 72°C is greater than that change at the melting point. This result suggests that the cubic modification of this substance may be a sort of the so-called plastic crystals.[4]

On the other hand, the transition point at 45°C was not found from our vapor pressure curves. Nelson[5] had already measured the vapor pressures below 72°C, but he could not

(1) C. Finback, *Tids. Kjmi. Bergwsen.*, **17**, No. 9 (1937)
(2) C. D. West, *Z. Krist.*, **88**, 195 (1934)
(3) I. Nitta, S. Seki, *J. Chem. Soc. Japan*, **62**, 581, (1941)
(4) According to the recent investigation by Aston and Pace, in the case of hexafluoroethane also the entropy change at transition point is greater than that at melting point. *J. Am. Chem. Soc.*, **70**, 566 (1948)
(5) Nelson, *Ind. Eng. Chem.*, **22**, 227 (1930)

also find the transition at this temperature.

Recently, Ivin and Dainton[6] have reported the measurement of vapor pressure of hexachloroethane without finding the lower transition point. From the accuracy of their apparatus they estimated that the enthalpy change at this transition point may be smaller than 700 cal./mol. Their data on vapor pressures are somewhat lower than our values, but much better agreement with ours than with that of Nelson when compared. It is also found from their results that the heat of transition at 72°C amounts to 1.9 ± 0.3 kcal./mol., which is in good agreement with our data, 2.07 kcal./mol.

It is now very desirable to determine the heat of transition at 45°C by the direct specific heat measurement. For this purpose and also as a part of our thermochemical investigation of plastic crystals, we have constructed a conduction calorimeter and measured the specific heats of this crystal. The details of experimental procedures may be described elsewhere. The obtained specific heat curves are represented in the accompaning figure and a part of the specific heats as well as heats of transition are indicated in Tables 1 and 2.

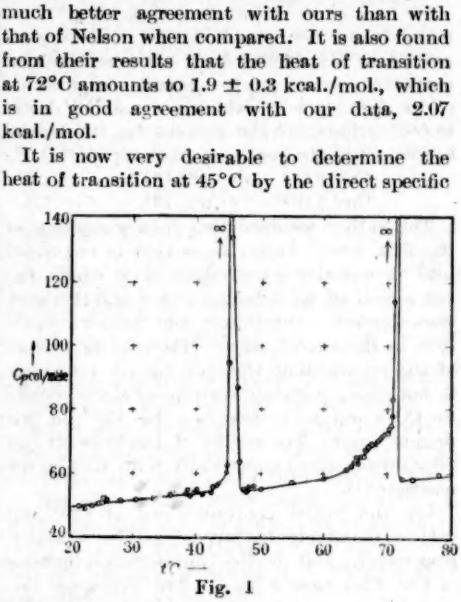

Fig. 1

Table 1
Specific heat of hexachloroethane

t°C	C_p cal./mol	t°C	C_p cal./mol	t°C	C_p cal./mol
22.25	48.9	45.80	110.7	67.47	68.8
23.45	49.7	43.05	95.9	68.18	68.6
24.55	51.5	46.55	86.5	68.48	69.3
25.35	52.1	46.75	63.0	68.85	69.1
35.95	52.9	47.45	54.8	69.09	70.9
37.85	53.4	47.70	54.2	69.45	71.0
38.51	54.8	47.95	55.3	69.90	71.7
39.35	53.3	48.55	55.9	70.14	73.3
41.12	53.0	48.95	55.0	70.50	74.2
42·90	55.7	50.00	54.7	70 63	77.2
43.25	56.4	55.05	55.7	70.85	82.6
44.58	59.9	60.0	57.7	transition	
44.75*	62.0	63.60	60.5		
45.40*	94.2	64.25	61.3	70.99	113.2
45.55*	328.7	64.65	63.0	71.02	175.3
transition		65.00	64.3	71.07	501.3
		65.35	62.0	71.50	307.9
45.00	253.9	65.70	64.4	72.70	57.1
45.15	213.8	66.05	64.4	73.80	57.3
45.25	173.8	66.40	66.9	78.00	58.7
45.40	133.5	67.10	67.7		

* superheating

Table 2

	t°C	ΔH cal./mol.	ΔS e. u.	ΔV cc./kg.
Transition	45.0	613[c]	1.93[c]	9.7
Transition	71.4	1965[c] {1900±300[a], 2070[b]}	5.70[c]	28.0
Melting	185	2330[d]	5.50[d]	—

a. K. J. Ivin, F. S. Dainton[6]
b. I. Nitta, S. Seki[3]
c. This research
d. Van der Lee

Since the transition at 45°C was found frequently to be superheated, we have measured the specific heat as slowly as possible (0.1°/minute) to avoid this. The observed magnitude of heat of transition at 45°C (613 cal./mol.) is in good agreement with that expected from the vapor pressure measurement by Ivin and Dainton and also by us. As shown in the figure, the upper transition is accompanied by the preceding gradual increase of specific heat. The heat of transition at 72°C (1.965 cal./mol) obtained by this direct method is also consistent with the data from the vapor pressure measurements.

In the table, the volume changes at transition points are also presented. We can see a very good parallelism between the entropy and the volume changes at these transition points.

For the theoretical treatment of the transition energies from the point of view of structual chemistry, it is necessary to determine the crystal structure more accurately. For this purpose, the X-ray analyses of these three modifications are now going on in this laboratory by other members and for the cubic form a model of molecular motions more precise than that of Hassel is gained. The discussion of the mechanism of the transitions may be postponed, to bring this investigation to completion.

In conclusion, the authors wish to express their sincere thanks to prof. Nitta for his kind guidance throughout this work. This study was helped by the Research Grant given by the Ministry of Education.

Department of Chemistry, Faculty of Science, Osaka University

(6) K. J. Ivin, F. S. Dainton, *Trans. Faraday Soc.*, **43**, 32 (1947)

Studies on the Ammoniacal Copper Solutions I
The Reaction Order of the Reduction by Carbon Monoxide and a Correction for the Escaping Carbon Monoxide

By Minoru HIRATA

(Received September 14, 1949)

It is a well-known fact that ammoniacal solutions of cuprous compounds absorb readily carbon monoxide.[1] Such solutions are used in determining carbon monoxide in gas analysis and for the purification of material gases in the ammonia manufacturing industry to remove carbon monoxide.

For the latter purpose, solutions containing both cuprous and cupric compounds are used circulating. In this case the absorbed carbon monoxide reduces cupric compounds in copper solutions and prevents the solutions from the increase of cupric compounds content which would be caused by the oxygen in material gases.

Hainsworth and Titus,[2] Larson and Teithworth,[3] Gump and Ernst[4] and Möller[5] studied on those solutions, but in spite of the importance of the reducing action of carbon monoxide the kinetics of the reduction were hitherto scarcely investigated. The present author has aimed to make clear this problem.

The compositions of the original copper solutions employed in the studies are shown in Table 1.

Table 1 (g./100 cc.)

Cu^{I}	Cu^{II}	NH_3	HCOOH	CO_2
8–15	1–5	8–16	2–10	6–13

Theoretical

It is verified that two mols of cupric copper are reduced by one mol of carbon monoxide and at the same time produce one mol of carbon dioxide. Though it is difficult to show the actual details of the reaction definitely, these experimental facts may be expressed by the following scheme,

$$2\,Cu^{II}+CO \longrightarrow 2\,Cu^{I}+CO_2 \qquad (1)$$

Here, Cu^{II} and Cu^{I} express the cupric and cuprous compounds respectively, whose chemical formulas have not yet been definitely determined.

According to the author's experiments, the reaction velocity of the reduction is proportional to each concentration of cupric copper and the absorbed carbon monoxide. Hence remembering the stoichiometric relation expressed by (1), it may be considered that the reduction occurs in two stages; the reaction of the first stage (2) which proceeds far slowly in comparison with the second stage (3) decides consequently the reduction velocity.

$$Cu^{II}+CO \longrightarrow Cu^{I}+CO^{*} \qquad (2)$$

$$Cu^{II}+CO^{*} \longrightarrow Cu^{I}+CO_2 \qquad (3)$$

The author assumed that in the reaction of the first stage carbon monoxide is converted into an unstable intermediate state which has lost a half of its reducing power and this substance causes immediately the further reduction in the second stage. Though the nature of the intermediate state of carbon monoxide is not clear, it should correspond electronically to CO^{+} and so is described by CO^{*} in the present paper. The results of reactions (2) and (3) coincide stoichiometrically with that of the reaction (1).

Let the initial concentrations of Cu^{II} and carbon monoxide be represented by a and b respectively, and let the concentration increase of Cu^{I} after time θ by x. The following two expressions may be given for the reduction velocity according to the above-mentioned reduction mechanism (1), and (2) and (3) respectively,

$$\frac{dx}{d\theta} = k^{III}(a-x)^2\left(b-\frac{x}{2}\right) \qquad (4)$$

and

$$\frac{dx}{d\theta} = k\,(a-x)\left(b-\frac{x}{2}\right), \qquad (5)$$

where k^{III} and k are the velocity constants respectively.

From the author's experiments, it has been known that k is nearly constant independently of the lapse of time, while k^{III} increases with it. Namely the reduction is of the second order.

In almost all of actual reactions, some of the absorbed carbon monoxide escape unreacted from solutions, therefore in such cases equation (5) should be corrected as follows,

$$\frac{dx}{d\theta} = k(a-x)\left(b-\frac{x}{2}-v\right), \qquad (6)$$

where v is the concentration of the escaped carbon monoxide during the time θ.

If it is assumed that the escaping velocity of the gas is proportional to its average concentration in the solution at that time,

$$\frac{dv}{d\theta} = k'\left(b-\frac{x}{2}-v\right) \qquad (7)$$

(1) Condamine, *Compt. rend.*, **179**, 691 (1925); Moser u. Hanika, *Z. anal. Chem.*, **67**, 448 (1926); D. R. P., 289694 (1914)
(2) *J. Am. Chem. Soc.*, **43**, 1 (1921)
(3) *J. Am. Chem. Soc.*, **44**, 2878 (1922)
(4) *Ind. Eng. Chem.*, **22**, 382 (1930)
(5) *Z. anorg. allgem. Chem.*, **224**, 113 (1935); ibid., **224**, 130 (1935)

is obtained, where k' is a constant characteristic of the reduction which we name the "exhalation coefficient".

When $b-\frac{x}{2} \gg v$, equation (7) should be strictly true.

From equations (6) and (7),

$$\frac{dv}{dx}=\frac{k'}{k}\cdot\frac{1}{a-x} \tag{8}$$

is obtained. Integrating equation (8),

$$v=-\frac{k'}{k}\ln(a-x)+\beta_1 \tag{9}$$

is obtained, where β_1 is an integration constant. At the initial state, $x=0$ and $v=0$, therefore,

$$\beta_1=\frac{k'}{k}\ln a \tag{10}$$

Inserting equation (10) into (9),

$$v=\frac{k'}{k}\ln\frac{a}{a-x} \tag{11}$$

If the value of v corresponding to any value of $a-x$ is known, that of $\frac{k'}{k}$ can be found out. Consequently the value of v against any arbitrary value of $a-x$ can be calculated.

By raising the temperature after the reduction is almost finished, the value of $a-x$ at the practical completion of reduction $(a-x)_{\theta=\infty}$ is obtaind. On the other hand, the value of v at that time $v_{\theta=\infty}$ is found out as the difference between the quantity of the carbon monoxide initially absorbed and the quantity expended in the reduction.

Then, from equation (11),

$$\frac{k'}{k}=\frac{v_{\theta=\infty}}{\ln\frac{a}{(a-x)_{\theta=\infty}}} \tag{12}$$

is obtained.

From equations (11) and (12), v is written as follows:

$$v=\frac{v_{\theta=\infty}}{\ln\frac{a}{(a-x)_{\theta=\infty}}}\cdot\ln\frac{a}{a-x} \tag{13}$$

In practical calculation, the cupric copper concentration $a-x$ with the lapse of time θ was observed, from which the $(a-x)$——θ curve was plotted. This curve was utilized for correcting the value of $a-x$ against θ, and this was necessary on account of the instability of copper solution.

Practically, velocity constants were numerically calculated instead of integrating equations (4), (5) or (6); for instance, equation (14) was adopted instead of equation (6),

$$\frac{x_i-x_{i-1}}{\theta_i-\theta_{i-1}}=\frac{1}{2}k\left(a-\frac{x_i+x_{i-1}}{2}\right)\left(2b-\frac{x_i+x_{i-1}}{2}-2v_i\right) \tag{14}$$

$i-1$ and i mean the successive numbers of measurements, and v_i is the value expressed by equation (15),

$$v_i=\frac{k'}{k}\ln\frac{a}{\left(a-\frac{x_i+x_{i-1}}{2}\right)} \tag{15}$$

Experimental

Experiments were made as follows; 70.0 cc. of copper solution was taken, and it was allowed to absorb a certain quantity of carbon monoxide. Then this solution was portioned 5.00 cc. each into several test tubes. The surface of the copper solution was always covered with liquid paraffin to prevent the evaporation of the solution, the loss of ammonia and carbon dioxide by escaping, and the oxidation of cuprous compounds by air.

The test tubes were dipped into a thermostat of the accuracy of ± 0.1°C, and the change of the cupric copper concentrations with the time elapsed was observed. It required 3 to 5 minutes for the contents of the test tubes to reach a certain temperature after dipping into the bath. At the end of the experiment, the last test tube was dipped into a water bath of 75°C for the period of 30 minutes to complete the reduction. In most cases, reduction was practically completed before the latter treatment was carried out. It was confirmed that the evaporation and the loss of copper solution and its spontaneous oxidation by diffusion of air would scarcely take place throughout the experiment.

The order of the reaction The two examples in which carbon monoxide scarcely escaped unreacted from the solutions are quoted in Tables 2 and 3. The small quantities of the escaped carbon monoxide were neglected, and k^{III} and k calculated using equations (4) and (5) are given.

Table 2 R. 61

No. of measurement i	Time θ_i min.	$\theta_i-\theta_{i-1}$ min.	Cu^{II}-conc. obs. g.mol/l.	Cu^{II}-conc. $a-x_i$ corr. g.mol/l.	x_i-x_{i-1} g.mol/l.	$\frac{x_i+x_{i-1}}{2}$ g.mol/l.	k^{III} g.mol/l. min.	k g.mol/l. min
0	0	—	0.508	0.508	—	—	—	—
1	5	5	0.453	0.453	0.055	0.028	(0.458)	(0.220)
2	10	5	0.423	0.419	0.034	0.072	0.439	0.190
3	15	5	0.388	0.393	0.026	0.102	0.470	0.191
4	20	5	0.374	0.374	0.019	0.125	0.467	0.179
5	30	10	0.345	0.345	0.029	0.149	0.516	0.181
6	50	20	0.310	0.310	0.035	0.181	0.595	0.195
7	90	40	0.280	0.280	0.030	0.213	0.750	0.221
8	150	60	0.275	0.275	—	—	—	—
9	300	150	0.275	0.275	—	—	—	—
10	∞	—	0.275	0.275	—	—	—	—

Initial concentration of CO : 0.1181 g.mol/l.
Reaction rate of CO : 98.7% Temperature of experiment : 50.0°C

Table 3 R. 64

No. of measurement i	Time θ_i min.	$\theta_i-\theta_{i-1}$ min.	Cu^{II}-conc. obs. g.mol/l.	Cu^{II}-conc. $a-x_i$ corr. g.mol/l.	x_i-x_{i-1} g.mol/l.	$\frac{x_i+x_{i-1}}{2}$ g mol/.	k^{III} g mol/l. min.	k g.mol/l. min.
0	0	—	0.512	0.512	—	—	—	—
1	5	5	0.462	0.462	0.050	0.025	(0.391)	(0.190)
2	10	5	0.434	0.429	0.033	0.067	0.383	0.170
3	15	5	0.404	0.403	0.026	0.096	0.414	0.172
4	20	5	0.379	0.382	0.021	0.120	0.452	0.177
5	30	10	0.349	0.352	0.030	0.145	0.464	0.170
6	50	20	0.316	0.316	0.036	0.178	0.512	0.171
7	90	40	0.287	0.287	0.029	0.211	0.552	0.161
8	150	60	0.275	0.275	—	—	—	—
9	300	150	0.275	0.275	—	—	—	—
10	∞	—	0.275	0.275	—	—	—	—

Initial concentration of CO : 0.1204 g.mol/l.
Reaction rate of CO : 98.5%
Temperature of experiment : 50.0°C

Now it is clear from the tables that k is constant independently of the time elapsed, while k^{III} increases with it and so the reducing reactions are of the second order.

The correction for the escaping carbon monoxide The results of the experiments where the escaping of carbon monoxide seemed pretty high, are given in Tables 5 and 6. In the last columns k calculated from equation (14) are tabulated. We can see that k calculated in such a way is constant enough through the whole course of each experiment. The compositions of the copper solutions used in the experiments are shown in Table 4.

Table 4

No. of experiment	Total Cu g.mol/l.	NH_3 g.mol/l.	HCOOH g.mol/l.	CO_2 g.mol/l.
R. 20	1.02	5.12	0.36	1.60
R. 70	0.30	1.04	0.10	0.31

Table 5 R. 20

No. of measurement i	Time θ_i min.	$\theta_i-\theta_{i-1}$ min.	Cu^{II}-conc. obs. g.mol/l.	Cu^{II}-conc. $a-x_i$ corr. g.mol/l.	$2v_i$ g.mol/l.	x_i-x_{i-1} g.mol/l.	$\frac{x_i+x_{i-1}}{2}$ g.mol/l.	k
0	0	—	0.463	0.463	0	—	—	—
1	2	2	0.448	0.448	0.001	0.015	0.008	(0.193)
2	5	3	0.443	0.439	0.002	0.009	0.020	0.0858
3	8	3	0.432	0.431	0.002	0.008	0.028	0.0818
4	13	5	0.421	0.419	0.003	0.012	0.038	0.0812
5	20	7	0.407	0.405	0.004	0.014	0.051	0.0777
6	30	10	0.387	0.388	0.006	0.017	0.067	0.0803
7	50	20	0.366	0.362	0.008	0.026	0.088	0.0846
8	90	40	0.330	0.330	0.011	0.032	0.117	0.0889
9	150	60	0.310	0.310	0.014	0.020	0.143	(0.0907)
10	300	150	0.305	0.305	—	—	—	—
11	∞	—	0.300	0.300	0.017	—	—	—

Initial concentration of CO : 0.0898 g.mol/l.
Reaction rate of CO : 90.8%
Temperature of experiment : 50.0°C

Table 6. R 70

No. of measurement i	Time θ_i min.	$\theta_i-\theta_{i-1}$ min.	Cu^{II}-conc. obs. g.mol/l.	Cu^{II}-conc. $a-x_i$ corr. g.mol/l.	$2v_i$ g.mol/l.	x_i-x_{i-1} g.mol/l.	$\frac{x_i+x_{i-1}}{2}$ g.mol/l.	k
0	0	—	0.102	0.102	0	—	—	—
1	5	5	0.093	0.093	0.001	0.009	0.005	(1.032)
2	10	5	0.086	0.087	0.003	0.006	0.012	0.987
3	15	5	0.083	0.083	0.004	0.004	0.017	0.896
4	20	5	0.077	0.080	0.005	0.003	0.021	0.924
5	30	10	0.077	0.076	0.006	0.0045	0.024	0.962
6	50	20	0.072	0.071	0.007	0.0045	0.029	(1.027)
7	90	40	0.068	0.068	—	—	—	—
8	150	60	0.068	0.068	—	—	—	—
9	300	150	0.077	0.068	—	—	—	—
10	∞	—	0.077	0.068	0.008	—	—	—

Initial concentration of CO : 0.0212 g.mol/l.
Reaction rate of CO : 80.3%
Temperature of experiment : 50.0°C

These facts seem to prove the above-mentioned assumption, equation (7), which was made for the calculation to correct the effect of the escaping carbon monoxide to be quite appropriate.

Summary

1. It is experimentally verified that the reduction of cupric copper by the carbon monoxide absorbed in the copper solution is a reaction of the second order.

2. In the calculation of the velocity constant for the reduction, it is found that the correction made for the carbon monoxide escaping unreacted, under the assumption that the escaping velocity of the carbon monoxide is proportional to its concentration in the solution at that time, is appropriate.

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LETTER

1, 2-Bis-(*p*-hydroxyphenyl)-1, 2-bis-(methylthio)-ethane, An Estrogenic Sulfur Analog of Hexestrol[1]

By Yoshiyuki URUSHIBARA and Michinori ŌKI

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In the programme of the survey of the possible estrogenic activity of hexestrol and stilbestrol analogs in which the members constituting the molecular skeletons of the well-established synthetic estrogens are replaced with other atoms or groups without altering the molecular shapes significantly, the discovery of a potent estrogen in 1, 2-bis-(*p*-hydroxyphenyl)-1, 2-dimethoxy-ethane, $HOC_6H_4CH(OCH_3)CH(OCH_3)C_6H_4OH$, an oxygen analog of hexestrol,[2] has naturally allured the authors to the synthesis of the corresponding sulfur analog, namely, 1, 2-bis-(*p*-hydroxyphenyl)-1, 2-bis-(methylthio)-ethane, $HOC_6H_4CH(SCH_3)CH(SCH_3)C_6H_4OH$.

The dibromide, m. p. 213-4°, from diacetoxystilbene was heated with methylthio-magnesium iodide, prepared by digesting sulfur with a Grignard reagent of methyl magnesium iodide or by passing methyl mercaptan into a Grignard reagent of ethyl magnesium iodide. The products were recrystallized from ethyl acetate. 1,2-Bis-(*p*-acetoxyphenyl)-1,2-bis-(methylthio)-ethane, $CH_3COOC_6H_4CH(SCH_3)CH(SCH_3)C_6H_4OCOCH_3$, was obtained in poor yields (10% or less of the theory) from the less soluble fractions. It melts at 118-9°, is soluble in methanol, acetone, acetic acid, and ethyl acetate, difficultly soluble in benzene and in chloroform, and almost insoluble in petroleum ether. Found: S, 16.86%; molecular weight, 374. Calculated for $C_{20}H_{22}O_4S_2$: S, 16.43%; molecular weight, 390.

The authors owe a more successful synthesis of 1, 2-bis-(*p*-hydroxyphenyl)-1, 2-bis-(methylthio)-ethane to I. W. Ruderman and E. M. Fettes[3] who have recorded a new preparation of thio-ethers. *p,p'*-Dihydroxy-hydrobenzoin (1.5 g.), $HOC_6H_4CHOHCHOHC_6H_4OH$, m. p. 219°, prepared by reducing *p*-hydroxy-benzaldehyde with sodium amalgam, was suspended in glacial acetic acid (75 cc.), methyl mercaptan (4 cc.) was added, and dry hydrogen chloride was passed into the mixture for two hours while methyl mercaptan (1 cc.) was added every quarter to make up for possible losses. The mixture was left to stand under a stopper for a couple of days. The crystalline deposits, and the crystals resulting in two or three days from the oil precipitated on pouring the mother liquor into water, were recrystallized from methanol-water. The substance thus obtained forms colorless needles, and on heating it melts at 193.5-5°, solidifies instantly, and then decomposes gradually and totally at 255°. Such a melting behaviour was not affected by recrystallization from pure methanol, acetone-water, or glacial acetic acid. Yield, 1.2 g. (65% of the theory). Found: S, 21.17%; molecular weight, 310. Calculated for $C_{16}H_{18}O_2S_2$: S, 20.93%; molecular weight, 306. The compound is easily soluble in methanol, acetone, and ether, sparingly soluble in benzene and in chloroform, almost insoluble in petroleum ether, and slightly soluble in boiling water. It precipitated a crystalline addition compound with mercuric chloride in saturated aqueous solution. Such a behaviour unlike a mercaptol

(1) A brief account was read by T. Takahashi before the annual meeting of the Chemical Society of Japan in Kyoto on April 2, 1950.

(2) Y. Urushibara and T. Takahashi, this Bulletin, **23**, No. 2 (1950), in press.

(3) *J. Am. Chem. Soc.*, **71**, 2264 (1949)

excludes a structure of the mercaptol of dihydroxy-desoxybenzoin, $HOC_6H_4CH_2COC_6H_4OH$, which might result from the dihydroxyhydrobenzoin. Further, acetylation with acetic anhydride and pyridine gave the same diacetate as obtained from diacetoxystilbene dibromide and methylthio-magnesium iodide.

In vagina smear test with ovariectomized mice 20 gammas of the free phenolic substance injected subcutaneously in two portions in oil solution produced oestrus in 67 percent, and 40 gammas in 100 percent, of the animals.

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